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Vol. 219 JANUARY, 1935 No. 1

THE CONTRIBUTIONS OF SCIENCE TO THE DEVELOPMENT OF THE MODERN GRAND PIANOFORTE.*

BY

GUY MARRINER.

Science, Art, Religion—these three are part of a whole in which there is no separation; for to do so is to limit. Humanity is suffering from an ignorance of the laws that govern; Religion is endeavouring to tell man what he is; Science is tapping, investigating that thought. Music is a mystery, a spiritual food, a vision of the unseen world. And Science has built bridges, the ladders and the means of transport to that realm.

A great physicist has said, "The structure of a modern grand pianoforte is a very simple matter compared with that of a single iron atom." But when we look at this superb instrument, the love of inventor and player, the construction of which has permitted a development on scientifically and mechanically correct lines, and realise that its 88 notes represent 2000 years of musical development and romance, I suggest we glance at history to see how art and science have been indispensable one to the other. As pianoforte-scale-designing is an exact example of applied physics, therefore a pianoforte designer must have a knowledge of mathematics, draughts-

* Presented at the Stated Meeting held Wednesday, October 17, 1934.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

manship and a full ripe complete knowledge of the branch of natural philosophy known as acoustics. This is because the art of pianoforte construction is the *art* of combining exact scientific knowledge with an instinct for practical craftmanship.

Now, as the whole range of musical instruments possess distinct features, so does the piano. Firstly, its cast steel strings are its vibrating system, secondly its felted hammers, action and keys are the mechanism for exciting that system, and thirdly its soundboard and bridges are the method of amplification; in other words the strings and soundboard are constructed from the *tone* viewpoint, and the hammers action and keys are the means for evoking that tone. As the piano is a fixed toned instrument, its scale is fixed by the maker; variations of what is called "temperament" are made possible by a tuner.

Besides tracing these developments, we shall see how science and art in their various stages of unfoldment, pushed each other on, and urged each other to greater heights of accomplishment. In every great tone creator in the past lived a superabundance of imaginative form which the instrument of the time could embody, and to which the instrument instantly strove to become equal. And in watching this growth, we should ever bear in mind man's development of the medium of expression—i.e., his fingers, which, in the passing of centuries, have manifested so much and become such perfect obedient servants to the tonal, touch, and technical demands of the composer and to the possibilities of the instrument, that each finger seems to acquire a sub-mind and sub-soul of its own.

The earliest prototype on record of the pianoforte is a Chinese instrument called the *Ke*, in 2650 B.C. The *Ke* was constructed of 50 strings stretched over a 5 inch wooden box. Each string was made of 81 silk threads, and was tapped with a padded hammer. Later the Chinese applied movable bridges on 25 strings to vary the pitch—these bridges were in groups of 5, each having a different colour; showing the Chinese understood the relation of colour to tone. The *Ke* is thus a primitive dulcimer, to which instrument we shall refer later on. The Chinese also had another instrument, the

Cheng, composed of several .ed pipes fixed into a bowl. When a *finger* covered a hole in the bamboo pipe, through which air passed, the pipe spoke. This is the earliest record we have of finger movement.

In 582 B.C. Pythagoras in Greece used a *Monochord* for experiments regarding the *mathematical* relations of musical sounds. You recall Pythagoras said "The world is built upon the power of numbers." A single catgut string was stretched over a wooden box. Under the string a strip of papyrus was glued to the top of the box, marked in sections and subdivisions corresponding to intervals of the scale. When the string was pressed and plucked, the tone produced was high or low, according to the place of the scale where the string was held. This Monochord was in universal use with the Greeks, and we read that in Roman churches it was used to sound the keynote for chorus singing.

An Italian Monk, Guido d'Arezzo, about the XI century, invented a movable bridge under the string of the Monochord, thus assuring a quicker and more correct intonation. Monochords were now built with more than one string, becoming Polychords. Guido d'Arezzo is credited with the invention of the do - re - mi system and the diatonic keyboard, and of having adopted a keyboard to polychord-stringed instruments. Each key (or clavis) had a tangent or pricker. As soon as the clavis was pressed the tangent would strike the string on the proper division of the scale, thus assuring the sounding of the correct tone required. Experiments on this order, and with a number of strings, during the XII and XIII centuries led to the *Clavicytherium*. In this instrument the strings, arranged in a triangular harp fashion, were made of catgut and were struck by a quill plectra at the end of the clavis. Invented about 1300 in Italy, it was copied in Germany.

Insomuch as the clavicytherium and other members of its immediate family, the Clavicymbal, Virginal, Harpsichord, Spinet are keyboard stringed instruments, they are not, virtually speaking, prototypes of the modern pianoforte. For stringed instruments which are *struck* are comprised of tangent action and hammer action and these, whose ancestor is the *clavichord*, are in no way to be confused with the plucked family; however this plucked family contributed various in-

dispensable ideas to the development of this noble instrument before you.

And so efforts to develop a singing tone brought forth in the middle of the XIV century the German Clavichord, which in its primitive stages was composed of 20–22 strings of brass made to vibrate, not by plucking or pricking, but by being agitated through pressure of a tangent—a brass pin flat on top—fastened to the key. It had more keys than strings, as the tangent, in striking, gave tone and pitch simultaneously. Most clavichords had two keys to one string (some had three) and two tangents were fastened to one key. Thus the performer had to manipulate the key to make each tangent strike at the proper place, hence all but the simplest compositions were almost impossible to perform. Towards the end of the XVI and beginning of the XVII centuries, the clavichord improved so much that it was the favorite keyed instrument of the period. It even maintained its supremacy during the XVIII century, long after the first appearance of the pianoforte. The range was extended to 50 and 77 keys, the soundboard covered half of the instrument—the part where the keys were located being open of necessity. Of course, the striking of a string produced a vibration during and after the key was released, and there was a consequent irritation of the sounding of the shorter part of the string when agitated by the tangent. So a strip of cloth was interlaced in that shorter part to deaden the sound. Also a damper was applied to the action, to silence the tone of the agitated string immediately the key was released. So here we have four vital parts of the modern Pianoforte in (1) the independent soundboard, (2) the metal strings, (3) the percussion—*striking* (not *plucking*) method of hitting the string—and (4) the application of a damper.

But the greatest improvement in the XVI and XVII centuries was a new method of tone production by which the clavichord became the first keyed instrument that enabled the artist to express individuality.

Now, a pin head hitting a brass wire couldn't have produced much quality or quantity or tone! In the ancient clavichords over which I have had the honour of running my fingers, the tone is amazingly small and weak, but it has a certain sweetness. The main contribution of this instrument

was something man yearned for in his soul, a sustained quality (however small) and a means of "expression." This was called "Bebung"—a trembling or shivering, which was a mournful sort of vibrato. It was only possible with the peculiar mechanism of the clavichord, where a tangent divided the string and simultaneously created the sound. . . . A *slight* relaxation of this pressure on the key lowers the pitch slightly, and a slight renewal of pressure heightens the pitch. But this delicate effect opened a new era in composition. Whereas earlier, stringed instruments had been used as an accompaniment to vocal (Church and secular) music, it was found a clavichord had possibilities of being a solo instrument through the modification of "touch." Even at that, "Bebung" did not satisfy. Musical compositions of that day became peppered with a sign—today obsolete—but which corresponds with our mordent, and also with "ornamentation." This threw into relief the dominating notes of a phrase, which Bebung could not prolong sufficiently. Turns, trills, appogiatura, grace-notes were some of the devices invented. Such embellishments were still further substitutes for prolonging the sustaining tone of a note.

Here we must pay a visit to the clavichord's cousins, the Harpsichord family, many features of which contribute to the evolution of the piano. Going back, in 1503 Spinetti of Venice constructed an oblong instrument of four octaves, which enabled him to use very long strings and a larger soundboard which covered nearly the entire space, thus increasing tone volume. The strings were pricked or twanged. The principle of this was that on the key was a "jack" with a centred tongue on top, and in this tongue was a quill attached to a spring. When the key was pressed, the point of the quill twanged the string through the upward movement of the jack, which fell back on release of the key. A bit of cloth attached to the jack dampened the string as the jack came down. The tone was wiry and nasal and had a sting to it, and responded to no expression from the artist. The loud tone made it popular. Small spinets were carried about and soon the keyboard, hitherto protruding, was built into the case. In England it became known as the Virginal, which, despite discussion, is not vitally different. It got its name supposedly from the fact

that either the Virgin Queen or the young virgins of the day found it as indispensable as the modern girl her lipstick.

At the end of the XVI century "*Virginals*" grew larger and were made harp-fashion, thus becoming the prototype of the upright piano. Europe, however, preferred the "winged" style of the harpsichord, the forerunner of the modern grand. The adoption of this form was dictated by the desire for greater volume of tone, bigger soundboard, more and longer strings—all these opened new fields for inventive genius. The tone became harsher more nasal, and offensive. *Desperate* attempts were made to attach a mechanical orchestra to it, devices imitating lute, flute, drums, cymbals, bells and so on. I have even seen an astonishingly grotesque conglomeration of effects which had 230 strings, 360 pipes, 105 tonal effects. It stood nearly 4 feet high and nearly 8 feet long, had two keyboards and—25 pedals! . . . Not so much in the English and German instruments as in the Italian and French of those centuries, does one find the exteriors lavishly painted and decorated, many of artistic merit, by eminent artists. Was this, too, a sign of desperation—an attempt to distract by means of the eye, the lack of tonal beauties within?

The only experiments of value were (1) the forte stop—which lifted dampers, (2) soft stop—pressed dampers on strings to stop vibration, (3) buff stop—soft cloth or leather between the jacks and strings, and (4) the shifting stop—shifting entire keyboard, a movement later applied to the transposing keyboard.

But as the frail cases couldn't stand heavy wire, and the quill couldn't make the strings sustain, harpsichords of two keyboards and with three strings to each note were built in the middle of the XVII century. No artistry for musician was possible; but the harpsichord gave the winged-formed case, two and three strings to a note, forte—piano pedal and the shifting keyboard to the embodiment of the modern piano.

Meanwhile the dulcimer had worked its way eastward, maybe through the Crusades, for it had long been known in Persia and Arabia. We have no sure knowledge that the Hebrew musical instrument named Dulcimer is the same as we know it, but the Hungarian gypsies use it today where it is known as the cymbalon. It is a trapeze shaped instrument,

3 feet in width, composed of a wooden frame enclosing a wrest-plank for the tuning pins. A soundboard with two or more sound holes carries the two bridges between which there are the lengths of wire intended to vibrate. Two, three and four strings are grouped for each note. The dulcimer, laid on a table or frame, is struck with hammers, the heads of which are covered on either side with hard or soft leather to produce loud or soft effects. There is no damping contrivance to stop the continuance of sound when not required. Hence a confused tone in loud sounds and a sweetness in soft tones.

And so the desire to combine the sustaining capacity of the clavichord with the power of the harpsichord and the sweetness of the dulcimer became that of musicians and inventors.

It can't be maintained that Johann Sebastian Bach, who lived from 1685 to 1750, treated the clavichord wholly individually, but he has helped individualise it nevertheless. At the beginning of the XVIII century genius itself couldn't release the instrument from being an accompanying one without running against the vocal spirit of the time. Bach regarded the clavichord as an individual instrument, and through his music the world understood instrumental as well as vocal music. Thus Bach was not so much a revolutionary as an evolutionary. Up to his time, clavichords had been tuned according to the Pythagorean comma, which is the difference of a semitone after the completion of the cycle of keys .... thus C is actually B♯ .... So to avoid this, the clavichord was relatively tuned—the well-tempered or well-tuned clavichord—the aim being an introduction of a system of tuning which should be sufficient for practical purposes, in which all the keys should be used indifferently and in their completeness. In order that a public recognition of this radical change should be established, Bach composed his "48" Preludes and Fugues in which every major and minor key was doubly treated with a prelude and fugue. This was epoch-making in the whole range of the art of music.

After observing prints and illustrations of musicians of those days and reading of their technique, it is apparent that the three middle fingers were used chiefly, the little finger less, and the thumb scarcely, if ever. It is in Bach's music that we realise the extent to which all five fingers were brought into

play. For previously no musician had manifested such dexterity in the network of partwriting. Hence the "48" Perludes and Fugues were Bach's creed in unity of composition, depth, originality and power. And on a Lilliputian instrument Bach composed his Gargantuan "48"—the Old Testament of every pianist; revealing to the world that clavier music was in itself a complete world, that the clavier, through Bebung and more than adequate compositions, could become capable of interpreting the whole of man's nature. If we play Bach today, we're inclined to imagine his fine effects are solely due to the perfection of the instrument. His music cries out for a subtle and expressive instrument—which he as little possessed, as Beethoven did show an orchestra suited to his ideas. "Because Bach was, the pianoforte is" has been truly written. Bach dreamed, and awakened the demure soul of the clavichord to an unknown fulness and he changed the mechanical force of the harpsichord to a sudden consciousness of personality. Therefore the new instrument—that which was to come—found its interpretation of what Bach prophesied and must have realised. The instrument of his day fell short of attainment, but such a prophet could surely be inspired to hear his music played in the years to come! Does a prophetic gift stop with speech alone? Surely the gift extends through other channels. . . . Likewise with the inventor; had he not equal vision, and with the infinite patience of greatness, know that one step should be taken at a time, and that every fundamental discovery would grow and bear fruit till the ultimate degree was expressed?

And so the need is felt. An invention is required to bring the expressive capacity of the clavichord into a line with the demands of genius. Hundreds of attempts had been made to make it more expressive. At the beginning of the XVIII century an artist named Hebenstreit played the dulcimer so perfectly that people were astounded at the new sound effects. Were men of science labouring to solve the problem by theoretical calculation, while it was solved in an unsuspected fashion before them, needing just an *impulse*, such as a world recognition of this virtuoso? Anyhow, at this time, the solution came! It came in the Hammerclavier or forte-piano, a

device in which the strings were struck by hammers in which every nuance of touch has grown to depend on the fingers.

And in order that the inspiration of this invention should not be lost, it was invented thrice over; in Italy by Cristofori in 1709, in France by Marius in 1716, and in Germany by Schroeter in 1717. Cristofori was curator to Ferdinand de Medici and had a superb collection of instruments, and was a builder of magnificent harpsichords. But his piano-forte, on account of its unaccustomed tone and touch, failed to gain any appreciable results at that time. . . . But there is now a monument to him in Florence, as the "Inventor of the Piano-forte."

Schroeter, on the other hand, together with his colleague Silbermann, known as the father of the German piano industry, worked so hard at the perfecting of the invention, that it gradually displaced the clavichord. Silbermann brought his model to Bach, who condemned the Schroeter action as being weak in the treble and too hard to play. This stimulated Silbermann, and later Bach commended wholeheartedly the improvements.

Six years after Bach's death, Mozart was born in 1756, and about that time until 70 years later came a period of the greatest activity in piano invention.

And how the world must have been waiting for it! How badly the world needed it! It is impossible to convey how tender these keyboards feel to our twentieth century fingers; a pressure of a butterfly's wing could almost press a key of a clavichord, and despite the fascination and grandeur of a three-manual harpsichord—such as Cristofori built—one's soul cries out for a medium that responds to mood temperament and spirit. In a survey of ancient instruments which I made this past summer in Germany, I was staggered by this need, and realised more than ever how the Masters wrote ahead of their time. For his day, Mozart wrote extremely difficult music for his instrument, Beethoven wrote notes in his sonatas that were not even on the piano at which he composed, so small was the range—he admitted he composed for the future—and the melodies of Schubert could never have conveyed on *his* piano the depth, tranquillity or ineffable beauty with which we hear them! Mozart, in 1777 in Vienna, got

terribly thrilled over the piano inventions of Silbermann's disciple, Stein, the inventor of what is known as the Viennese mechanism. This received the name of Viennese action when his children came to Vienna and there with Streicher built up the world-renowned busines. Stein was a genius. Listen to part of Mozart's letter: "I must now begin at once with Stein's pianoforte. They 'damp' much better than Regensburg instruments. If I strike hard, whether I let my fingers lie on the key or lift them, the sound is over and done with the very instant I lift my hand. I may come down on the keys as I like, the tone never hangs fire; it doesn't get weaker or stronger or stay on; it's all just *one*. His instruments have this point that makes them better than others: they are made with an *escapement* which there isn't a man in a thousand knows anything of; without that it is just impossible for a piano to help blocking or sounding again. His hammers fall back the very moment they touch the strings whether you hold them or not. When he has finished a piano, he sits and tests all kinds of passages, runs and leaps works and scrapes till the piano'll do anything. For he works only for the good of music, and not his own merely, or he would have been done for long ago. Stein says 'If I didn't love music so passionately, or couldn't do a little on the piano, I should long ago have lost all patience in my work. But I'm just a lover of instruments which don't try the player and which will last.' They *do* last too. He puts the sounding board in air, rain, sun, snow or any beastly thing to warp it and then glues cross bars in it until it's strong and firm. He's quite glad when it warps, for you're quite sure nothing more can happen to it. He often cuts it and glues it and so makes it strong. The machine moved by knees [pedal of that day] is also better made by him than others. I scarcely touch it when off it goes, and as soon as I take my knee away the least bit, you can't hear the slightest sound."

There was a pioneer! And subsequently numberless small modifications and improvements were introduced in key-levers, hammers, dampers, escapements, pedals, strings, sounding board—each scientific discovery of which may have been a life-time's work for the inventor. How abundant and unfaltering was their faith! In their patience and fortitude

they foresaw how the world would someday be given the fullest expression of their creations through the perfected pianoforte.

The great French, English, American and Austrian piano factories can almost all be traced back to Germans. The Parisian Erard and Playel were founded by Germans. Steinway emigrated from Brunswick over here. Zumpe carried his hammerclavier to England, and there the houses with Broadwood at their head effected the improvements which have resulted in the appropriation of the name 'English' to the mechanism of Silbermann.

After 1820, when Stodart of London and New York perfected a system of a metallic bracing for a grand piano, and in 1825 when the full iron frame was invented by Alpheus Babcock, pianoforte construction becomes an international cooperation in a most exciting way. Piano tone was still thin and wiry, keys were smaller and depth of quality was slight, breaks in the scale, uneveness in the different registers, false harmonics (caused by improper scale designing) were still outstanding faults when Chopin was composing his ethereal music and his cascades of precious stones. There was a demand for a larger tone and consequently heavier stringing, when a most important contribution was made by Sebastian Erard. A French aristocrat, living in London, he invented the "compound-escapement-action" allowing transference of utmost power and individuality, for the slightest release of pressure of the key enables the jack to clear itself.

I regard this invention as essentially important to pianoforte playing, and hope to illustrate it at the close of this lecture.

In 1855 there was a sensation at the World's Fair in New York when Steinway exhibited a square piano with an overstrung scale (giving greater string length) together with an iron frame, and overcoming the harsh metallic quality of tone. Thus the "Battle of the Iron Frame" was won. Since then there has been a tremendous advance in every way. Tone is richer and fuller, more vital. With the accumulation of knowledge of acoustics, an understanding has become general of the complex vibrations which are the basis of beautiful tone.

Let us briefly look at this instrument in its various parts. The pedals give command over every variety of colour and

gradation of tone. The middle or sostenuto pedal gives a power of using selected notes undamped. *Aliquot scaling* is one in which an unstruck string is added to the higher treble notes, the object being amplification through co-vibration. Though little volume is added, this is in accoradnce with the proper application of the natural laws of acoustics. When a grand piano is soft-pedalled, the whole instrument is immediately converted into what is the same as aliquot scaling.

The designing of an iron frame is an engineering problem. The total stress on a piano frame can exceed 20 tons which however, due to overstringing, is not a direct pull.

The variable factors in the production of the 88 notes are (1) the length of the vibrating part, (2) the tension to which this is subjected, (3 and 4) the diameter and the density of the wire used. Every detail of piano construction is hinged upon the lay-out of the Wrest Plank scale, the Bridge scale and the Hitch pin scale, and these, in turn, are based upon the strike point of each string. Wires are made of cast-steel, of great tensile strength. 30 bass notes have steel cores and a copper loading as a compensation for necessary loss of length. The demand for a tone which is full, clear and round, which has volume and which can be sustained, has been met by use of perfectly circular wire, capable of withstanding a strain of over 200 pounds. The breaking strain of good piano wire is over 150 tons per square inch!

Every available kind of skin and leather was tried as a cover for hammers, until the most suitable, merino sheep wool felt was applied, and even then much experimenting had to be done before the final smooth elasticity and resistance were obtained. A piano *toner* produces the best quality of tone of which a piano is capable. This is a matter of instinct and experience in relaxing undue strain of felt covering of hammers without affecting the elasticity of the striking face. The modern keyboard of 12 notes to the octave has stood a test of 600 years, yet the central problem of intonation is insoluble. That tiny interval the "Pythagorean comma" can't be eliminated! Do you realise that this (5th interval) is flat? and that this (major 3d) is sharp?

Sound is known as an effect caused by undulations of air on the drums of the ear. Sound waves, like the swell of the

sea, are series of pushes of air particles. If a piano string was isolated from the soundboard, very little sound would be heard. The soundboard harnesses the strings and they energise a large surface of board, which in turn moves large zones of air—with the result of increased loudness of sound and not increase of energy. The modern soundboard is so perfect that it reinforces these vibrations without any change of character. So, really, it is the nervous system of the piano. The wood of the soundboard is either Norway spruce or white pine—these were found to be the best after much experimenting. The curvature in the soundboard retains the elasticity and responsiveness.

The train of mechanism which transmits to the strings the impetus given by the player's touch is the *action*. Differences of touch affect the vibration of the string and so the ultimate tone. It was Cristofori, as I have remarked, the Paduan harpsichord maker, who first created the machinery through which the impetus of the finger could be transmitted to the string *and so produce either loud or soft tone*. His discovery permitted the jack to 'escape,' an individual damper was provided for each note, and a 'check' was added. The grand-action of today is substantially that of Erard. The compound-escapement-action is much too complicated to attempt to explain, but like four-wheel brakes on a car, it ensures absolutely the immediate and instantaneous obedience of the action to the finger.

During the past five years an entirely new field in science has been available for inventors. I refer to the radio. Many people are under the impression that radio has made inroads on other musical instruments and upon artists. One cannot deny that altogether. (Perhaps the hammerclavier did upon the clavichord!) But out of radio has arisen a benefit in the electro-acoustic tools, without which I am told, the explorer and investigator of the piano could not possibly have progressed in the phenomenal way he was recently. So far the soundboard has benefited greatly. During the past year, Steinway have produced an accelerated action. The key, hitherto poised on a flat surface bearing, caused considerable friction where the key was pressed. A round bearing has been substituted for the flat, and the system of key weighting has

been shifted. This gives the key a rapid and firm return, together with a lighter touch.

I here quote part of a letter from Mr. Paul Bilhuber, the inspired inventor of Steinways in New York.

"The pianoforte maker has always sought the reduction and elimination if possible of such forces as friction and inertia in the moving parts of key and action, in order to avoid the dissipation of energy. In the new action, the easier, more sensitive and therefore more responsive 'feel' has been brought about by a reduction in the friction loss in the key bearing. . . . An improvement—a further improvement—based on the principle of preventing energy loss has been applied to the support of the treble strings. An electrically treated and hardened scale rib under the capotasto bar permits a much sharper edge—like an ideal knife edge." The benefits of this are threefold. He writes that they are "(1) Greater freedom of vibration of string, (2) truer scaling as the string lengths are more precise, (3) augments the effect and function of the front duplex scale, insuring a clearer tone, and eliminates the fuzziness and jingling sometimes found in older instruments." The recognized leader of Philadelphia music, Dr. Leopold Stokowski, offers his contribution to this talk. He said to me a few days ago that nothing is outside the scope of scientists, for the potentiabilities of orchestral instruments are so little developed really. And while he approves of all that Science is doing in the way of analysis, he feels the time has come when the synthetic element needs to be developed. . . . The next step he feels is to be one of synthesis—an extensive linking up—which I understand to be perhaps a cosmic—an all-inclusive philosophy.

In these amazing inventions, which include the compound escapement action of Erard, I am inclined to believe that science has offered art a test for dexterity. Science has compelled the artist to train his hand to the mechanical perfection of the action. Science has made the artist listen with new ears, feel the keys in new ways with infinite varieties of touch, *and with a new sensation in the hand.* How else can one account for that divine singing quality we sometimes hear of so great artists? The piano—the result of two centuries of scientific labours and faith—with the perfectly trained hand of the

artist clear all channels so that the message flows direct from the soul of the artist to the soul of the hearer.

If music, as proved, has been given to the world through the mind of man, apart from instruments adequate for giving the means of expression, how much more can Science prove that laws are waiting just outside our human mechanism, and will be expressed when we understand with greater clarity the laws that govern us and that govern Life? . . .

Science! Art thanks you for the possibilities you have extended to create new tonal unfoldments, newly coloured interpretations, and instruments of glory that transmute and transform the Star of Inspiration—in the universal sharing of man's work on this planet—*humanising the divine.*

An Alchemistic Mystery Explained.—R. STREBINGER AND W. REIF, in *Mitt. Numismat. Ges. Wien*, **16**, 209–13, tell how applied microanalysis solved the mystery connected with a Kaiser Leopold I. medallion belonging to the Vienna Collection. This curious piece of metal was reputed changed from silver into gold in 1677. A close examination revealed that the medallion had been dipped into some liquid, the mark of the meniscus being plainly visible. The immersed portion showed a gold color, the rest silver. Microanalytical determinations made on various points on the medallion show it to be an alloy of 47% gold, 44% silver, 7% copper and the rest tin, zinc and iron. An alloy of this composition changed from a silver to a gold color upon dipping into a 1 : 1 aqueous nitric acid.

C.

Retarding Mold on Grapes During Transit.—(U.S.D.A. Clip Sheet No. 850.) The Department has found a cheap and effective method of retarding the development of mold on grapes, either in transit or storage, without injuring their taste or appearance. This new method consists in the use of 10 grams (about $\frac{1}{3}$ ounce) of sodium acid sulphite or sodium metabisulphite placed in pads at the bottom of the ordinary grape "lugs" or mixed with the sawdust in which the fruit is packed. These chemical compounds give off sulphur dioxide slowly, providing an extended fumigation with extremely low concentrations of gas.

C.

Nature-Debased Coins.—(*Science Service.*) Archeological excavations on the island of Cyprus recently brought to light a number of copper Greek and Roman coins which, according to all records, should have been made of silver. A thorough examination disclosed that these coins were silver after all, the copper apparently having been plated on during their period of entombment. Dr. S. G. Willimott, government analyst at Cyprus, was able to show that the copper coats were put on by the galvanic action due to the chance contact of silver coins with a less noble metal, iron, in the presence of water containing copper sulphate as an electrolyte.

C.

THEORY OF THE ALTERNATING-CURRENT BOLOMETER.

BY

PARRY MOON,

Massachusetts Institute of Technology.

Various devices have been used in radiometry: the thermocouple, the bolometer, the photoelectric cell, the radiometer. The several forms of radiometers suffer not only from their fragility but also from a certain inflexibility of the method, due to the necessity of applying the radiation to the actual moving system. Photoelectric devices are extremely valuable for rough measurements, but even the best of present photoelectric cells are found to be unreliable [1] unless used for the rapid intercomparison of two sources, as in the color analyzer of A. C. Hardy.[2]

A process of elimination leaves the thermocouple and the bolometer, both of which have been used by numerous investigators. Apparently the two are inherently capable of the same order of sensitivity; but the thermocouple, because it requires less auxiliary equipment, has been highly developed in the last few years, while the bolometer has almost dropped into oblivion. I shall attempt to show, however, that the bolometer is well adapted to operation on alternating current, resulting in an instrument of interesting possibilities.

The measurement of small amounts of radiant power by either thermocouple or bolometer is a difficult task, requiring for its accurate accomplishment sensitive instruments and a highly refined laboratory technique. Among the difficulties which beset the investigator are:

(*a*) Difficulties inherent in the use of high-sensitivity galvanometers.

(*b*) Effects due to spurious e.m.f.'s generated by slight temperature differences at the various circuit junctions.

[1] Also photoelectric cells cannot be used for measurements at wave-lengths beyond about 1.2 μ.

[2] "A New Recording Color Analyzer," paper presented before the Optical Soc. of Am., New York, Feb. 24, 1934.

If the measurement of radiant power is to be placed upon an engineering basis comparable with the precision measurement of electrical quantities, it is essential that the above difficulties be eliminated. D.-c. amplification by means of vacuum-tubes is entirely impracticable with the thermocouple or the bolometer because of the low voltages which are obtainable. If, however, a means can be found for obtaining an alternating or a pulsating e.m.f. instead of the customary steady e.m.f., then a multi-stage a.-c. amplifier can be used. Such amplifiers have been highly developed and can be built for the measurement of voltages as low as 10^{-8} volts.

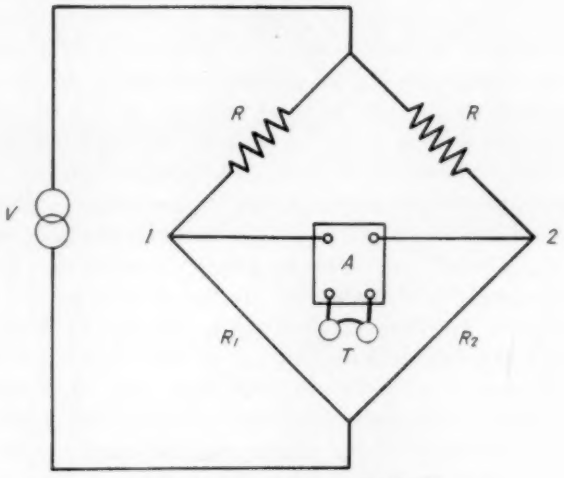
A possible method is the use of a motor-driven shutter which causes a periodic fluctuation in the irradiation of a thermojunction. By using a junction of extremely low heat capacity and a low frequency of fluctuation, the generated e.m.f. will tend to follow the variations in the irradiation, and the a.-c. component can be amplified. Such a scheme is being used by Professor L. Harris at Massachusetts Institute of Technology.[3] Another solution of the problem consists in the use of an ordinary thermocouple and a steady radiation, the pulsation being introduced by a periodically-varying circuit parameter. The thermocouple, for instance, may be connected in series with a fixed resistance and a motor-driven variable condenser. An amplifier connected across either the condenser or the resistance will be supplied with a pulsating e.m.f., the alternating component of which is directly proportional to the radiant power absorbed by the thermojunction. Both of the above schemes eliminate difficulty (*a*), and the former method also eliminates (*b*). It is evident, however, that all such methods suffer from the fact that the radiation is not being used in the most effective manner. The greatest possible single-frequency rms voltage which can be obtained at the amplifier input is only 45 per cent. of the direct voltage obtainable under the same conditions.

It occurred to the writer that disadvantages (*a*) and (*b*) could be eliminated, as well as the above conversion loss, by the use of a bolometer operated from an a.-c. source instead of from the customary d.-c. source. The change is an obvious

[3] "Thermocouples for the Measurement of Small Intensities of Radiation," Phys. Rev., **45**, 1934, p. 635.

one, but a search of the literature failed to reveal a previous suggestion of this kind. The arrangement is shown in Fig. 1 where a source of alternating voltage V supplies the bolometer bridge. The bridge consists of two equal non-inductive resistances (R, R) and two identical bolometer wires (R_1) and (R_2), one of which receives radiant power. A tuned amplifier (A) is connected between 1 and 2 and operates an a.-c. milliammeter, a pair of head phones (T), or other device.

FIG. 1.



Circuit diagram of bolometer bridge.

The customary bolometer used in the past consisted of two identical platinum tapes in an evacuated container, one side of each tape being blackened to absorb radiant energy. Such a bolometer can, of course, be used equally well on alternating current. With any practicable size of strip and a sufficiently high frequency, the cooling during a cycle is negligible; and if the customary direct current of i amps. be replaced by an alternating current of i rms amps., the temperature distribution along the strip will be exactly the same in the two cases. Consequently a given irradiation will produce a rms voltage between 1 and 2 equal to the direct voltage obtained in the d.-c. case (with d.-c. galvanometer disconnected). Evidently the conversion loss obtained with the a.-c. thermocouple is entirely

absent in the a.-c. bolometer. Also difficulties (*a*) and (*b*) are eliminated: the galvanometer has been replaced by a rugged apparatus, and spurious e.m.f.'s have no effect on the tuned detector. Furthermore, since a potential-operated device of high input impedance is used across *1* and *2*, the voltage actually obtained is considerably higher than if a low-resistance galvanometer is connected across these points.

Evidently the use of a high-impedance detector opens up new possibilities in bolometer design. In the a.-c. bridge, the resistance of the bolometer strip has no effect on the detector; and thus it becomes possible, for the first time, to use advantageously bolometer wires of extremely high resistance (even thin sputtered metal strips), resulting in greatly increased sensitivity. In the tape bolometer it is obvious that radiant energy falling near the ends of the tape is not used to best advantage because of heat conduction through the tape to the supports which are at room temperature. By using a long tape, blackened only in the center portion which is irradiated, conduction loss is greatly reduced. It would seem that conditions could be further improved by using a bright wire of circular cross-section instead of a tape, and attaching a small blackened target at the center of the wire. Such a construction reduces radiation loss to a minimum. The bolometer wires are, of course, operated in a vacuum to eliminate convection loss. With the vacuum target bolometer, then, there remains only the radiation loss from the small target—a loss which cannot be eliminated, though it can be reduced in some cases by using a selectively-radiating target having low emissivity at long wave-lengths and high emissivity in the band of wave-lengths to be measured.

The present paper develops the theory of the vacuum target bolometer for use in the a.-c. bridge circuit. The treatment is confined to bolometers with bright wires [4] and blackened targets and is based on the assumption that the radiation from the surface of the wire is negligible in comparison with that from the target. The condition of $R \gg R_1$ is also used since it results in maximum sensitivity. Data on the characteristics of such bolometers and the method of design are given and it is shown that the sensitivity obtainable with

[4] Not necessarily of circular cross-section.

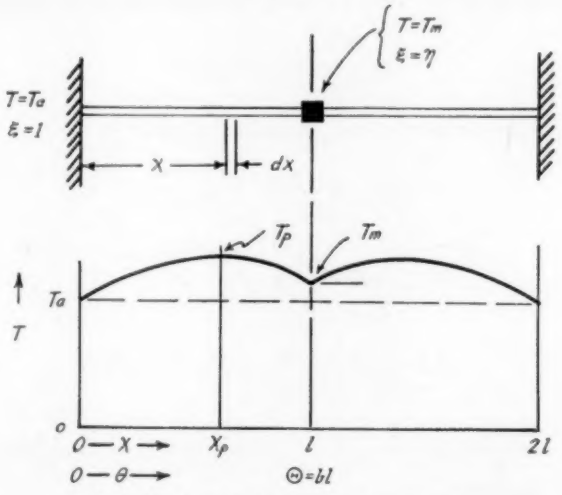
the a.-c. bolometer is at least as high as that of the best thermocouples.

Because of this high sensitivity and the freedom from troubles experienced by other radiometric devices, the a.-c. bolometer offers practical advantages in spectroradiometry and photometry. In spectroradiometry, it is hoped that the high sensitivity will be found of service and that the ruggedness of the equipment will help place such measurements on an engineering basis. In photometry the a.-c. bolometer with a suitable filter offers a reliable device for precision measurements, free from the well-known serious objections which can be raised against both visual and photoelectric methods.

2. THE DIFFERENTIAL EQUATION AND ITS SOLUTION.

Consider a polished wire of length $2l$ and of cross-sectional area a (Fig. 2) and assume that there is no radiation from the

FIG. 2.



Temperature variation along a bolometer wire.

wire or from the rear surface of the target. The front surface of the target is assumed to be perfectly black.

T = temperature (° K.) of the wire at a distance x from the end,

T_a = ambient temperature,
T_m = temperature of target,
T_p = maximum temperature,
i = current flowing through wire (rms amps.).
σ = resistivity (ohm-cm.). It is found that the resistivity of platinum is essentially proportional to the absolute temperature.

Thus

$$\rho = \alpha T.$$

Also,

k = thermal conductivity (watts cm.$^{-1}$ deg.$^{-1}$),
S = area of one side of target (cm.^{2}),
σ = Stefan-Boltzmann constant = 5.709×10^{-12} watts cm.$^{-2}$ deg.$^{-4}$,
G = watts/cm.^{2} of radiant power incident on the target.

Consider a length dx of wire at distance x from the end. The heat gained per sec. by this element by conduction is

$$ka\frac{d^2T}{dx^2}dx \quad \text{(watts)}.$$

The heat generated per sec. by the current is

$$\frac{i^2\rho dx}{a} = \frac{i^2\alpha T dx}{a} \quad \text{(watts)}.$$

Thus,

$$\frac{d^2T}{dx^2} + \frac{i^2\alpha}{a^2k}T = 0. \tag{1}$$

It is convenient to introduce the new variables:

$$\xi = T/T_a, \qquad \theta = bx, \qquad \text{where} \qquad b = \frac{i}{a}\sqrt{\frac{\alpha}{k}}.$$

Then (1) becomes

$$\frac{d^2\xi}{d\theta^2} + \xi = 0, \tag{1a}$$

whose solution is

$$\xi = A\cos\theta + B\sin\theta, \tag{2}$$

where A and B are constants of integration.

Boundary Conditions—No Irradiation.

$$\text{When} \begin{cases} \theta = 0, & \xi = 1. \\ \theta = bl = \Theta, & \xi = \eta, \end{cases} \qquad \text{where} \qquad \eta = T_m/T_a.$$

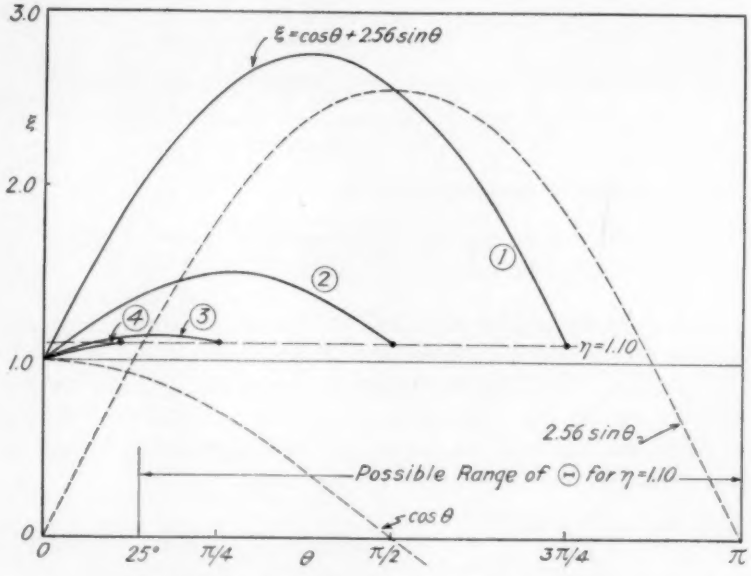
Substitution in (2) evaluates the constants A and B, and thus

$$\xi = \cos\theta + \left(\frac{\eta - \cos\Theta}{\sin\Theta}\right)\sin\theta. \tag{2a}$$

Eq. (2a) gives the temperature at any point along the wire in terms of the two parameters η and Θ.

It will be noted that the temperature is expressed as the sum of two terms: a cosine term and a sine term, as shown in Fig. 3. Evidently the solution has physical significance only

FIG. 3.



Temperature variation along a bolometer wire, $\eta = 1.10$.
1. $\Theta = bl = 3\pi/4$.
2. $\Theta = \pi/2$.
3. $\Theta = \pi/4$.
4. Impossible case with positive slope of curve at $\theta = \Theta$.

in the range $\cos^{-1}(1/\eta) < \Theta < \pi$. The latter limit is of course fixed by the fact that both terms become negative at $\theta = \pi$. The former limit is dependent upon the requirement

that in a target bolometer receiving no radiation the heat must flow into the target to supply the radiation loss, and thus the $(\xi - \theta)$ curve must have a negative slope as $\theta \to \Theta$. For small values of Θ, the coefficient of the sine term is comparatively small and the maximum temperature is only slightly above the target temperature. As Θ is increased by increasing the length of bolometer wire, decreasing its cross-sectional area, or increasing the current, the coefficient of the sine term increases rapidly and the maximum temperature rises. As Θ approaches π, the sine term approaches infinite amplitude.

The location of the point of maximum temperature is easily obtained by differentiating eq. (2a) and equating to zero, which gives

$$\theta_p = \cos^{-1}\left[\frac{\sin\Theta}{\sqrt{\eta^2 - 2\eta\cos\Theta + 1}}\right]$$

or

$$x_p = \frac{a}{i}\sqrt{\frac{k}{\alpha}}\cos^{-1}\left[\frac{\sin\Theta}{\sqrt{\eta^2 - 2\eta\cos\Theta + 1}}\right](\text{cm.}) \qquad (1)$$

and the maximum temperature is

$$T_p = T_a\frac{\sqrt{\eta^2 - 2\eta\cos\Theta + 1}}{\sin\Theta}. \qquad (4)$$

It has been found convenient to express the foregoing equation in terms of the bolometer design parameters η and Θ. The current i can also be found in terms of the same parameters by use of the conditions at $\theta = \Theta$. Since, for thermal equilibrium, the heat radiated by the target must equal the heat conducted to the target by the wire,

$$-ka\left[\frac{dT}{dx}\right]_{x=l} - \frac{\sigma S}{2}(T_m^4 - T_a^4) = 0$$

or

$$\left[\frac{d\xi}{d\theta}\right]_{\theta=\Theta} + \frac{\sigma S T_a^3}{2kab}(\eta^4 - 1) = 0. \qquad (5)$$

But from (2a),

$$\left[\frac{d\xi}{d\theta}\right]_{\theta=\Theta} = -\sin\Theta + (\eta - \cos\Theta)\cot\Theta.$$

Thus,

$$-\sin\Theta+(\eta-\cos\Theta)\cot\Theta+\frac{\sigma ST_a^3}{2i\sqrt{\alpha k}}(\eta^4-1)=0$$

or

$$i=\frac{\sigma ST_a^3}{2\sqrt{\alpha k}}\frac{(\eta^4-1)\sin\Theta}{(1-\eta\cos\Theta)}\text{(rms amps.)}. \tag{6}$$

The resistance of one bolometer wire is

$$R=\frac{2}{a}\int_0^l\rho dx=\frac{2\alpha}{a}\int_0^l Tdx=\frac{2\sqrt{\alpha k}T_a}{i}\int_0^\Theta\xi d\theta \tag{7}$$

or, substituting (2a),

$$R=\frac{2\sqrt{\alpha k}T_a(1+\eta)}{i}\frac{(1-\cos\Theta)}{\sin\Theta}. \tag{7a}$$

The Irradiated Wire.

The original differential equation still applies, subject to the boundary conditions:

$$\text{When}\begin{cases}\theta=0, & \xi=1,\\ \theta=\Theta, & \xi=\eta+\delta,\end{cases}$$

where δ is the small increment in η caused by the absorption of radiant energy by the target. Thus the temperature of the irradiated wire becomes

$$\xi=\cos\theta+\left(\frac{\eta+\delta-\cos\Theta}{\sin\Theta}\right)\sin\theta. \tag{8}$$

Also at $\theta=\Theta$

$$\frac{GS}{2}-kabT_a\left[\frac{d\xi}{d\theta}\right]_{\theta=0}-\frac{\sigma ST_a^4}{2}[(\eta+\delta)^4-1]=0$$

or, neglecting higher powers of δ,

$$\left[\frac{d\xi}{d\theta}\right]_{\theta=\Theta}+\frac{\sigma ST_a^3}{2i\sqrt{\alpha k}}[\eta^4+4\eta^3\delta-1]-\frac{GS}{2i\sqrt{\alpha k}T_a}=0. \tag{9}$$

But differentiation of (8) gives

$$\left[\frac{d\xi}{d\theta}\right]_{\theta=\Theta}=-\sin\Theta+(\eta+\delta-\cos\Theta)\cot\Theta. \tag{10}$$

If i remains the same, independent of irradiation, which is a condition easily obtainable in practice by making the resistance of the bridge ratio arms high in comparison with the resistance of the bolometer wires, then it is permissible to use the previous value of i given by eq. (6). Substituting (6) in (9) and utilizing eq. (10), one obtains

$$\delta = \frac{G(1 - \eta \cos \Theta)}{\sigma T_a^4[4\eta^3 - (3\eta^4 + 1) \cos \Theta]}. \tag{11}$$

The rms voltage appearing across the amplifier input is equal to the differences in IR-drops in the two bolometer wires, or from (7*a*),

$$\Delta V = 2\sqrt{\alpha k} T_a \left(\frac{1 - \cos \Theta}{\sin \Theta}\right)[(1 + \eta + \delta) - (1 + \eta)].$$

Substitution of the value of δ from (11) gives

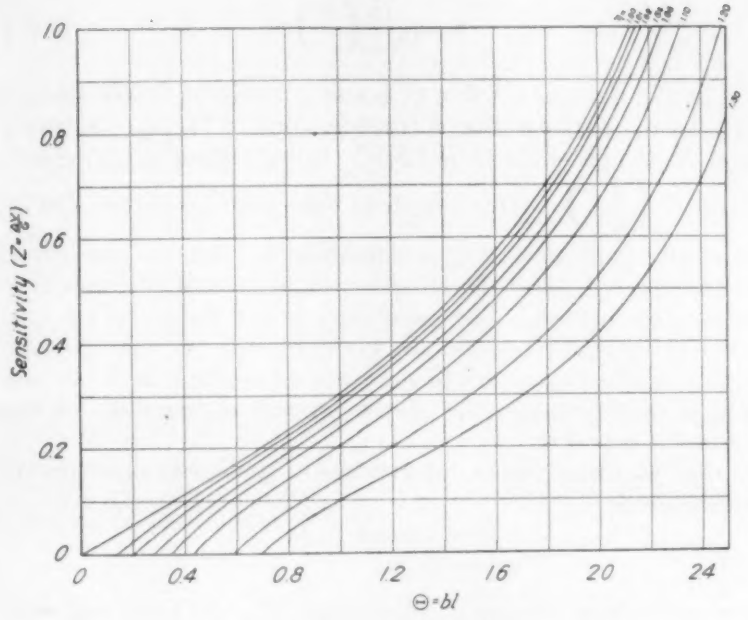
$$\Delta V = \frac{2\sqrt{\alpha k}}{\sigma T_a^3}\left(\frac{1 - \cos \Theta}{\sin \Theta}\right) \times \frac{(1 - \eta \cos \Theta)G}{[4\eta^3 - (3\eta^4 + 1) \cos \Theta]} \text{(rms volts)}. \tag{12}$$

Since ΔV is directly proportional to the irradiation G, it is convenient to define the sensitivity z of the bolometer as the voltage produced across the amplifier input divided by the watts/cm.^{2} of the radiant power producing this effect. Thus,

$$z = \frac{\Delta V}{G} = \frac{2\sqrt{\alpha k}}{\sigma T_a^3}\left(\frac{1 - \cos \Theta}{\sin \Theta}\right) \times \frac{(1 - \eta \cos \Theta)}{[4\eta^3 - (3\eta^4 + 1) \cos \Theta]} \text{(volts watt}^{-1} \text{ cm.}^2\text{)}. \tag{13}$$

Curves have been computed by eq. (13) and are given in Fig. 4. It will be noted that the sensitivity tends to increase as η decreases, which reduces the radiation loss from the target. Also the sensitivity increases rapidly as (bl) is increased. It should be pointed out, however, that the high values of z predicted for $\Theta \to \pi$ cannot be realized in practice due to radiation from the surface of the wire.

FIG. 4.



Sensitivity of vacuum target bolometer.
$T_a = 293.0°$ K.
$\alpha = 0.0366 \times 10^{-6}$.
$k = 0.7000$.
$\sigma = 5.709 \times 10^{-12}$.

3. DESIGN OF BOLOMETERS.

It has been convenient to express all quantities in terms of the two parameters, η and Θ, the former being the target temperature referred to ambient temperature and the latter being directly proportional to the length of the bolometer wire. In the design of a bolometer, therefore, the following equations are needed:

From eq. (6),

$$\frac{S}{i} = \frac{2\sqrt{\alpha k}}{\sigma T_a^3} \frac{(1 - \eta \cos \Theta)}{(\eta^4 - 1) \sin \Theta}. \qquad (6a)$$

Also from the relation:

$$i\left(\frac{l}{a}\right)\sqrt{\frac{\alpha}{k}} = \Theta,$$

we obtain

$$\frac{l}{a}S = \sqrt{\frac{k}{\alpha}}\left(\frac{S}{i}\right)\Theta. \tag{14}$$

In the design, a value of η and a value of Θ are selected arbitrarily, perhaps after a consideration of Fig. 4. Substitution in (6*a*) gives the ratio (S/i). Substitution in (14) gives a value of $\left(\frac{l}{a}S\right)$. The length of wire and the target size are generally fixed, at least approximately, by physical conditions; so the current i and the cross-sectional area of the wire a are easily determined. The sensitivity is calculated by eq. (13), while other characteristics are given by eqs. (3), (4), (7*a*), and (11). If the characteristics are not as desired, or if the wire size is unobtainable, the above process is repeated for new values of η and Θ.

For platinum wires, an average of available experimental results gives

$$\alpha = 0.0366 \times 10^{-6},$$
$$k = 0.700.$$

For an ambient temperature of 293.0° K., the foregoing equations become

$$S/i = 2.228\frac{1 - \eta\cos\Theta}{(\eta^4 - 1)\sin\Theta} \tag{6b}$$

$$\frac{l}{a}S = 4372\left(\frac{S}{i}\right)\Theta, \tag{14a}$$

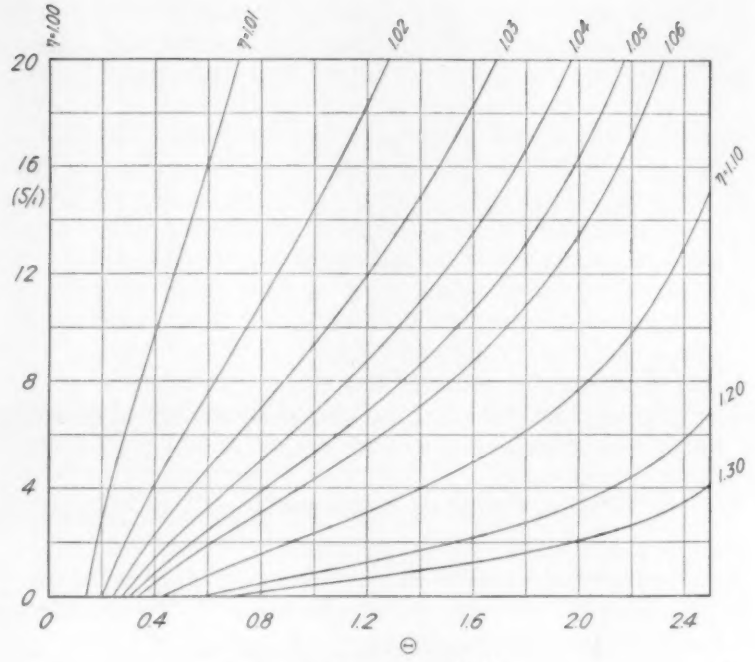
$$z = 2.228\left(\frac{1 - \cos\Theta}{\sin\Theta}\right)\frac{(1 - \eta\cos\Theta)}{[4\eta^3 - (3\eta^4 + 1)\cos\Theta]}, \tag{13a}$$

$$T_p = 293.0\frac{\sqrt{\eta^2 - 2\eta\cos\Theta + 1}}{\sin\Theta}. \tag{4a}$$

To facilitate bolometer design, values of (S/i) and $\left(\frac{l}{a}S\right)$ have been computed for platinum wires and $T_a = 293$, and the results have been plotted in Figs. 5 and 6.

The question arises as to the possibility of further increase in sensitivity by change of materials, target size, ambient

FIG. 5.



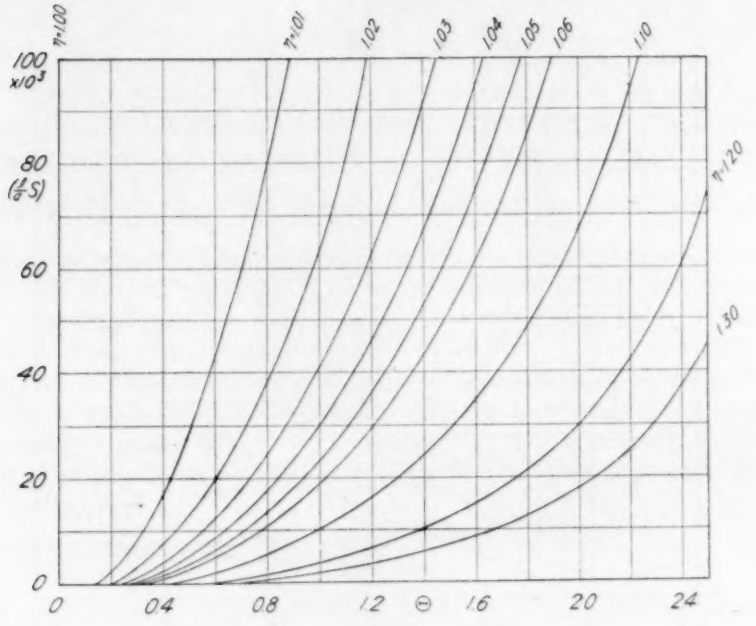
(S/i) Ratio for vacuum target bolometer.

$T_a = 293.0°$ K.
$\alpha = 0.0366 \times 10^{-6}$.
$k = 0.7000$.
$\sigma = 5.709 \times 10^{-12}$.

temperature, or other factors. For given values of η, Θ and T_a, eq. (13) shows that the sensitivity varies as the square root of (αk). But the (αk) product is practically the same for all pure metals, and thus from the standpoint of sensitivity it makes little difference what metal is used as long as it is pure. Platinum, because of its high melting point, its ductility, and its low emissivity, is particularly good; while alloys are unsuitable because of their low values of (αk).

Since S does not appear in eq. (13), the target size has no effect on the sensitivity (when the latter is expressed in volts produced per watt/cm.^{2}). In a uniform radiation field, the voltage cannot be increased by increasing the target size. The physical reason for this conclusion is that though the

FIG. 6.



$\left(\frac{l}{a}S\right)$ Ratio for vacuum target bolometer.

$T_a = 293.0°$ K.
$\alpha = 0.0366 \times 10^{-4}$.
$k = 0.7000$.
$\sigma = 5.709 \times 10^{-12}$.

absorbed energy increases directly with S, the radiation loss also increases in the same ratio; and since convection and conduction losses are negligible in the vacuum target bolometer, the sensitivity remains independent of S. Of course if only a small area is irradiated, as when the output slit of a monochromator is imaged on the target by means of a lens, the above conclusion does not apply and the target should be no larger than necessary.

A reduction in ambient temperature results in a marked increase in sensitivity. Eq. (13) shows that at the temperature of solid CO_2, the bolometer has twice the sensitivity obtainable at room temperature for the same value of η and Θ. Similarly, at the temperature of liquid nitrogen the sensitivity is increased by a factor of approximately seventeen. The

improvement is due to a reduction of radiation loss. Such an improvement is always possible with bolometers or thermocouples; but, because of practical difficulties, the reduction in ambient temperature is usually considered only as a last resort.

Another possibility of increasing the sensitivity is by using a target surface which radiates selectively. Since the target temperature is rarely above 350 K., the radiation from the target will be entirely in the infrared, with a maximum beyond 8μ. If it happens that the radiation to be measured lies in a wave-length band remote from 8μ, a selectively-radiating surface may result in a considerable increase in sensitivity. For example, Dr. A. H. Pfund [5] has found that in some cases targets coated with evaporated bismuth black absorb almost perfectly in the visible region but have low emissivity beyond about 2.5μ. The subject is worthy of further investigation.

4. BOLOMETER CIRCUITS.

The circuit of Fig. 1 may be used with a milliammeter at T, and the radiant power may be measured by reading the output meter. For precision work, however, it seems advisable not to rely upon the constancy of the amplifier but to employ a compensation method. An alternating voltage of known and variable magnitude may be introduced into the grid circuit of the first amplifier tube from a voltage divider. The radiation is measured by adjusting the voltage divider until a balance is indicated by T, and the value of G is then directly proportional to the reading of the voltage divider. A continuous record can be obtained, if desired, by using a motor-driven voltage divider operated by the amplifier output. By obtaining the compensating voltage from the same source that supplies the bolometer bridge, voltage variations in V will cause but slight errors. Variations in the amplifier have, of course, no effect on the readings.

A third possible mode of operation is to restore balance as in the ordinary Wheatstone bridge by readjusting the current in one of the wires. In the bolometer bridge, however, condi-

[5] "Methods of Blackening Receivers," paper presented before the Optical Society of America, Feb. 23, 1934.

tions are complicated by the heating effect of the current. The method seems to have numerous disadvantages and will not be discussed in the present paper.

5. ASSUMPTIONS.

In the interest of mathematical simplicity, several assumptions have been made in the foregoing theory. They will now be examined in greater detail.

One assumption is that there is no appreciable periodic fluctuation in the temperature of the wire and target due to the use of alternating current. A rough analysis indicates that with a target 2×10^{-4} cm. thick used at 1000 cycles/sec., a temperature fluctuation of as much as 0.01 C. is possible. It is not at all apparent if such a variation will change the sensitivity appreciably. In practice, however, temperature fluctuations can always be made negligible by using a thicker target or a higher frequency.

A second assumption is that the target coating is perfectly black at all wave-lengths. Insofar as the absorbed energy is concerned, the assumption introduces no appreciable error since black-coatings of evaporated bismuth, antimony, and other metals can be made which absorb over 99 per cent. of the incident radiant energy over a fairly broad band of wave-lengths. As pointed out in §3, however, coatings having low emissivity at wave-lengths near 10μ may result in a considerable *increase* in sensitivity beyond the calculated values.

The principal assumption is that radiation from the wire is negligible. Since the radiating surface of the wire is generally small compared with that of the target and since the emissivity of bright platinum at the temperatures usually encountered in bolometer practice is only about 0.04 compared with approximately 1.00 for the target, it might appear that the assumption is thoroughly justified. This is undoubtedly true for the lower values of Θ; but if an attempt is made to boost the sensitivity by increasing the current, the maximum temperature of the wire may reach high values while the target remains only slightly above room temperature. Under these circumstances, the assumption may lead to large errors.

It is easily shown that the rigorous equation for the vacuum bolometer is

$$\frac{d^2\xi}{d\theta^2} + \xi - c(\xi^4 - 1) = 0, \tag{15}$$

where c is a constant depending upon the radiating properties of the wire surface. For zero emissivity of the surface, $c = 0$ and the equation reduces to (1), whose solution may be written:

$$\xi_a = \cos\theta + \left(\frac{\eta - \cos\Theta}{\sin\Theta}\right)\sin\theta. \tag{2a}$$

The effect of c is best taken into account by using a perturbation method. The solution of (15) is written as

$$\xi = \xi_a + \Delta,$$

where Δ is the small difference between the true solution and the approximate solution. Substitution in (15) gives a new differential equation:

$$\frac{d^2\Delta}{d\theta^2} + (1 - 4c\xi_a^3)\Delta - c(\xi_a^4 - 1) = 0, \tag{16}$$

which can be solved for any given case. The sensitivity can then be calculated by methods which need not be considered here. Numerical investigation of a design using a drawn platinum wire 10μ in diameter and 2 cm. long with a target of 0.02 cm.^{2} area showed that a sensitivity of 0.20 was easily obtainable. This compares favorably with the best values for thermocouples and does not by any means represent an upper limit for the bolometer. The complete investigation of the a.-c. bolometer by use of eq. (16) is now under way and it is hoped that the results can be presented in the near future. The present paper is justified by the facts that

(*A*) The approximate solution gives a picture of the whole range of bolometer characteristics and allows the calculation and design to be carried out in a simple manner for the lower values of Θ.

(*B*) For large values of Θ, the approximate solution still serves as a basis for the perturbation method.

6. COMPARISON OF THE BOLOMETER AND THE THERMOCOUPLE.

Since the alternating-current bolometer must compete with present radiation thermocouples, it is interesting to compare the sensitivity of the two devices. The theoretical maximum sensitivity obtainable with a vacuum thermocouple is easily found by neglecting the heat loss through the wires leading to the active junction. Using a target of area S attached to the junction, the radiation loss is

$$\sigma(T^4 - T_a^4)S, \quad \text{(watts)}$$

where T = temperature of target = $T_a + \Delta T$. Introducing the condition that $\Delta T \ll T_a$ and equating to the received power (GS), we obtain

$$\frac{\Delta T}{G} = \frac{1}{4\sigma T_a^3}$$

or

$$z = \frac{E_t}{4\sigma T_a^3}, \tag{17}$$

where E_t = volts produced by thermocouple per deg. temperature difference.

For a constantan-manganin couple such as the Moll vacuum thermocouple, $E_t = 40 \times 10^{-6}$, and for $T_a = 293°$ K.,

$$z = 0.070.$$

Evidently this represents an upper limit to the sensitivity obtainable with radiation thermocouples made of these two metals. Table I gives theoretical maxima for several other metals. Information is also given for a commercial thermocouple which is advertised as the most sensitive on the market.

A mere consideration of the open-circuit voltage, however, does not tell the whole story. If the thermocouple is used with a galvanometer, the voltage appearing across the terminals of the latter for conditions of optimum power transfer will be only one-half the open-circuit voltage. If an a.-c. amplifier is used, the effective voltage is reduced even more, due to the conversion loss discussed in §1. As to the voltage sensitivity of the two devices (galvanometer and a.-c. amplifier), there seems to be no great difference. A representative

TABLE I.
Sensitivity of Thermocouples and Bolometers.
(Ambient temperature = 20° C.)

	$S_{(cm^2)}$.	Calories/Sec. for 1 μv.	μv/deg.	$\frac{\pi}{(\text{volt watt}^{-1}\ \text{cm.}^2)}$.
Constantan-manganin Vacuum thermocouple (theoretical maximum)			40	0.070
Bismuth alloy Vacuum thermocouple (theoretical maximum)			120	0.21
Burt vacuum thermocouple*	0.006	1×10^{-8}	120	0.14
Tellurium-bismuth Vacuum thermocouple (theoretical maximum)			400	0.70
A-C. Vacuum bolometer (easily-obtainable value)				0.20

* C. H. Cartwright, *Rev. Sci. Inst.*, 1, 1930, p. 602.

high-sensitivity d'Arsonval galvanometer having a coil resistance of 16 ohms gives one mm. deflection at one meter with 1×10^{-7} volts. Considerably smaller voltages can be detected by the Coblentz galvanometer or by the use of two galvanometers in tandem, as in the Moll thermo-relay and the Pfund resonance radiometer. All such methods are inherently limited by the Brownian movements so that it is doubtful if under ordinary conditions one can possibly detect voltages below 10^{-8} or 10^{-9} volts.[6] Vacuum-tube amplifiers are also limited, in this case by molecular agitation in the resistors and by tube noise, to very nearly the same voltage.[7]

[6] This is true of the Moll thermo-relay, according to Ornstein, Moll and Burger, "Objektive Spektralphotometrie," Braunschweig, 1932, p. 17. The resonance radiometer minimizes the effect of Brownian movement, so that J. D. Hardy has found it possible, under very special conditions, to detect voltages as low as 10^{-11}. Some of the difficulties may be inferred from his statement (*R. S. I.*, **5**, 1934, p. 120): "The resonance radiometer . . . had been set up in the second basement . . . upon one of the piers which support the building. . . . The supports for the galvanometer had been tested with a mercury surface and found to be very free from mechanical vibrations late at night, during more or less quiet weather. At these times a remarkable degree of mechanical steadiness could be obtained, and it was during such periods that the recording was carried on."

[7] According to Mr. E. A. Johnson, Massachusetts Institute of Technology, the best present practice allows the detection of 10^{-9} volts, though it is possible that further improvements resulting in greater sharpness of tuning may better this value.

TABLE II.
Minimum Detectable Radiation.

	$G_{min.}$ (watts/cm.^{2})
With Galvanometer.	
Constantan-manganin thermocouple	29×10^{-9}
Bismuth alloy thermocouple	9
Burt thermocouple	14
With a.-c. amplifier	
Bismuth alloy thermocouple	24
Tellurium-bismuth thermocouple	7
A-C. Bolometer (easily obtainable value)	5

Table II, therefore, is computed on the basis that either galvanometer or a.-c. amplifier can detect 10^{-9} volts. It is also assumed that the galvanometer resistance is equal to the thermocouple resistance and that with the a.-c. thermocouple the single-frequency rms voltage obtainable at the amplifier input is 20 per cent. of the steady thermocouple e.m.f. obtainable under the same conditions. Under these conditions it will be noted that the tellurium-bismuth couple with a.-c. amplifier can detect 7×10^{-9} watts/cm.^{2} while the bolometer detects 5×10^{-9}.

Tables I and II are based on a uniform radiation field of G watts/cm.^{2}. In case the radiation is confined to a narrow pencil, however, the comparison still holds provided the targets are the same size in all cases. It has been convenient sometimes to use multi-junction thermocouples. Evidently the multi-target a.-c. bolometer is equally feasible; and since high resistance has no effect on the response of the a.-c. amplifier, such a construction offers advantages in some cases.

The above discussion indicates that the a.-c. bolometer compares favorably in sensitivity with the best radiometric devices which have been produced. In comparison with the thermocouple and galvanometer, it also possesses the very decided practical advantage of eliminating the effects of spurious e.m.f.'s and of obviating the need for special vibrationless supports and mountings; while in comparison with the a.-c. thermocouple it has the advantages of comparative ease of construction and absence of rotating parts.

In conclusion, I wish to thank Mr. E. A. Johnson, Professor L. Harris, and Professor D. C. Stockbarger, who read the manuscript and made valuable suggestions.

THE INTENSITY OF THE HIGH FREQUENCY ELECTRODELESS DISCHARGE AS CONDITIONED BY POWER CONTROL OF THE GENERATOR.

BY

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In the excitation of a gas by means of electrodeless discharge it is essential to differentiate between that type which is predominantly caused by a high frequency electromagnetic field (ring discharge) [1,7] and that which at low pressures is obtained by means of an electrical field (glow discharge).[2] In the latter case the gas may be placed in a cylindrical or spherical container which is introduced either into an electrical field as formed between parallel condenser plates or the electrical field associated with a loosely-wound air-core solenoid, excited by high frequency current with just sufficient potential so that the electromagnetic field is not intense enough to excite the ring discharge.

This work deals with the excitation of hydrogen when it produces a uniform glow discharge due to its presence, at low, constant pressure, in a high frequency electrical field.

In order to approach the subject from a quantitative point of view we wish to limit the external conditions imposed on the gas. The gas will be confined in an electrodeless cylindrical pyrex tube, 2 cm. in diameter, placed coaxially into a loosely-wound air-core solenoid, excited to produce an undistorted high frequency electrical field. With these restrictions, the variables that still enter into the production of the discharge are: amount of gas, the electrical field strength as conditioned by the h.f. current in the solenoid, and the differ-

[1] J. J. and G. P. Thomson, "Conduction of Electricity through Gases," Vol. II, 431, 1933, Camb. Univ. Press.

[2] For a summary see K. K. Darrow, "High Frequency Phenomena in Gases," First Part, *The Bell System Tech. Jr.*, **11**, 576 (1932) and Second Part, ditto, **12**, 91 (1933), also "Electrical Phenomena in Gases," Williams and Wilkins Co., 1932.

ence of potential existing across its ends for a given frequency of the exciting oscillating circuit. To these must be added the characteristics of the driving circuit and the harmonic content of the oscillating circuit of which the solenoid and the glowing gas forms an integral part. It is to the neglect of these latter factors that much of the unreproducibility of electrodeless discharge data may be attributed.

METHOD OF GENERATING THE H.F. ELECTRICAL FIELD.

Continuous wave excitation was employed. A dynamically balanced push-pull vacuum-tube circuit was used. A thousand volt direct current generator connected to a potential divider provided the power supply. A previous investigation,[3] using high current density, had shown that an air-core solenoid excited under these conditions produced a magnetic field in every detail comparable to the magnetic field produced by a direct current. Since the uniformity of the magnetic field intensity in the central third of the solenoid is enhanced and extends more and more to the ends of the coil with decrease in excitation current, it should follow that the electrical field associated with it would conform to the same variations except in so far as such a field may become predominant at low current density due to the interwinding difference of potential. This latter is a maximum at the ends of the solenoid L_1 and a minimum at the center, as shown in Fig. 1. The solenoid L_1, under the subsequent working conditions, is tuned to current resonance,[4] and the R. F. Ammeter A_c shows the magnitude of this current.

Townsend and Donaldson [5] have shown and MacKinnon [6] has verified the fact that this type of solenoid can develop under high frequency excitation and low current density a predominant electrical field.

To test the applicability of their deductions to our design of oscillator we introduced a coaxial cylindrical discharge tube, 2 cm. in diameter, and 30 cm. in length, into the field of an eight turn, 22 cm. long and 9 cm. diameter solenoid and

[3] O. Stuhlman and S. Githens, *R. S. I.*, **3**, 561 (1932).
[4] M. Jezewski, *Zs. f. Phys.*, **48**, 123 (1928).
[5] J. S. Townsend and R. H. Donaldson, *Phil. Mag.*, **5**, 178 (1928).
[6] K. A. MacKinnon, *Phil. Mag.*, **8**, 605 (1929).

surrounded the tube by a water jacket 0.5 cm. thick. Upon filling the inner tube with hydrogen and striking the glow at a given frequency, potential, and gas pressure, it was found that a bluish glow, blunt and cigar-shaped, was formed at the middle fifth cylindrical section of the vacuum tube. If now the current through the solenoid is increased, the bluish glow gradually elongates symmetrically along the length of the tube and can be extended beyond the edges of the solenoid. That part of the glow extending beyond the solenoid is of a lighter blue color and appears to cap the main body of the glow, at both ends. It is the gradual fading of this cap at its apex that gives the glow a cigar-shaped contour. Under these circumstances the quartz window at the end of the tube becomes fluorescent. This, as in a similar case described by Herzberg,[7] can be attributed to the collision of the hydrogen ions with the quartz window, since they are moving under the difference of potential existing between the ends of the solenoid and the surrounding grounded objects. Upon short circuiting the ends of the coil, the discharge is extinguished, so that the coil is comparable to an oscillating open pipe with a node at the middle. An ammeter inserted at this point, *Ma*, shows upon proper balanced tuning, no current flow.

Upon reducing the current, the glow uniformly contracts from both ends towards the center of the tube, where it eventually collapses and suddenly extinguishes.

If the water jacket around the fully glowing discharge tube is gradually filled, it will be noticed that the contraction of the glow is analogous to that described above, due to the resulting decrease in current and its accompanying decrease in field strength. Since the presence of the water can only increase the effective dielectric constant and hence decrease the electrical field strength, it follows that this glow as here presented is of pure electrical origin but subject to the electrical characteristics of the oscillating circuit.

CHARACTERISTICS OF THE EXCITING H.F. FIELD.

Before using the electrical field to excite an electrodeless discharge it is essential to know to what extent the intensity

[7] G. Herzberg, *Ann. d. Phys.*, **85**, 553 and 565 (1927).

and uniformity of this field are determined by the constants of the circuit.

Its uniformity is determined by the dynamic balance of its push-pull symmetry; its intensity by the drop in potential across its terminals and its harmonic content.

The most disturbing of these, in any large frequency range, are the ever-present harmonics and their influence on the electrical field of force. If the natural frequency of the oscillator is high and the harmonics follow each other at short intervals, then the field of the solenoid which follows these variations is only interpretable in a qualitative way, due to the discontinuities that exist when these harmonic frequencies are excited. If, however, the harmonic spacing is large, then a section between two harmonics may be used. A constant field intensity in this frequency range can, however, only be obtained if the power supplied by the generator to the oscillator is constant. Unfortunately, this power is a function of the frequency to which the oscillator is excited. The electric field of the solenoid is a part of this oscillating system and it in turn is conditioned by the dielectric in the core of the solenoid. If, therefore, the oscillator is tuned to a given frequency and if now a gas is introduced into the vessel at a pressure so that the glow can be struck, a decrease in distributed capacitance of the solenoid with its implied increase in dielectric constant of the material in the core occurs. Hence the oscillator must be retuned. If this retuning is omitted when changes, contributed by successive stages of excitation of the gas, are encountered with the accompanying changes in dielectric constant, it will be found that this is an additional cause for not being able to obtain reproducible results.

If now the current through the solenoid is increased and with it the intensity of the electrical field and as a consequence the intensity of the glow discharge is enhanced, it does not follow that this increase in current is accompanied by a proportional increase in the power supplied by the generator. The neglect of this non-linear interaction between oscillator and driver has resulted in much confusion in the interpretation of the literature on the electrodeless discharge.

Results possessing a quantitatively interpretable value, must therefore be obtained with constant power applied by

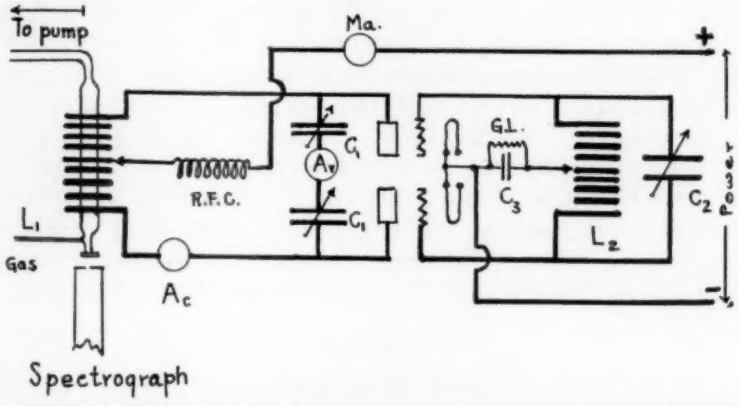
the driver to the oscillator and the resulting h.f. electrical fields must further be limited to frequency ranges free from harmonics.

TECHNIQUE.

The frequency range under investigation extended from 5.0 to 7.5 mega-cycles. The power range of the driver used in this work extended from 10 to 100 watts. The hydrogen was excited to glow in the above 2 cm. tube, at pressures in the neighborhood of 250 microns. The glow discharge at these pressures was of a bluish pink color with the molecular spectrum more intense than the Balmer lines. The Fulcher lines were very prominent. At low field strengths the Balmer lines were just visible and increased in intensity with increase in field strength, thus gradually contributing the characteristic rose-colored glow to the gas.

The gas was introduced at the end of the tube, Fig. 1,

FIG. 1.



Push-pull oscillator. L_1 plate inductance, solenoid under discussion, showing electrodeless cylindrical tube in position, quartz window facing spectrograph. L_2 grid inductance. C_1 plate condenser, National Type D.X., 3000 V., 440 mmf. C_2 grid condenser, ditto. C_3 grid condenser, 500 V., 0.002 mf., mica fixed. *GL* 500 ohms. A_c radio-frequency ammeter, *Ma* ditto milliammeter. Two fifty watt Radiatrons (UV 203 A). Generator 1000 V., d.c. A_r radio-frequency ammeter used in connection with Townsend's method to determine difference of potential across terminals of L_1.

facing the spectrograph and evacuated at the other end after passing through a baffle immersed in solid CO_2. Since an electrodeless discharge is very sensitive to the faintest traces of impurities, a direct-vision spectroscope can be used to examine the discharge for the presence of traces of mercury

vapour and the impurities accompanying the entering hydrogen. A very pure grade of electrolytic hydrogen, under pressure, was obtained from steel storage tanks. The gas was slowly passed through glass baffles immersed in solid CO_2 before entering the discharge tube. The hydrogen spectrum, free from obvious impurities, was photographed on "Wratten M. Plates" with intensity markers and photometered with a Moll Microphotometer. The photographic blackening of the Balmer lines was converted by means of these markers into intensity values. The power supplied by the generator, the current in the solenoid at a given frequency, and the photographic exposures were all made coincidently with the gas at constant pressure.

Preliminary observations had shown that in this design of oscillator the drop of potential across the solenoid as measured by Townsend's method,[5] was directly proportional to the current A_e flowing through the solenoid.

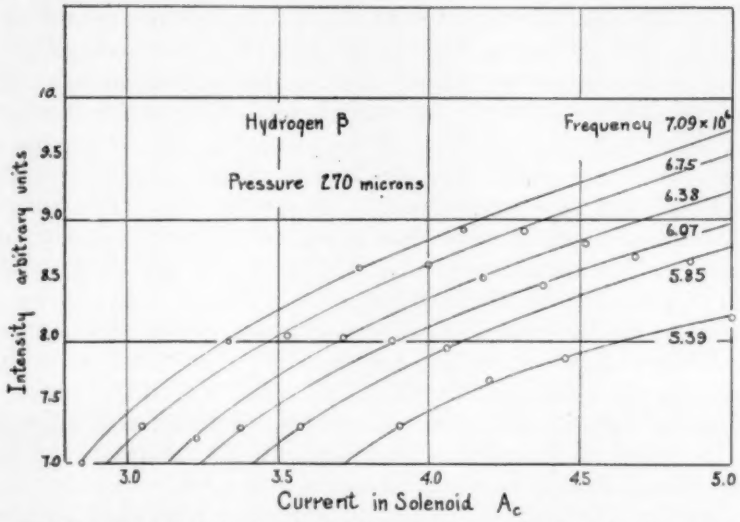
The frequencies were measured with a Standard Wave Meter so loosely coupled to the solenoid that its natural frequency did not produce a measurable current distortion in the oscillator. Its readings were reproducible within 0.1 meter. The current through the solenoid (A_e) was obtained by means of a "Weston H.F. Ammeter," error 3 per cent. for the scale deflection. The milliammeter and voltmeter on the power control of the driver were accurate to 5 per cent. for any scale reading. The pressures were kept constant within 3 per cent. Maximum variations in measured intensities of the spectral lines were not greater than 5 per cent.

RESULTS.

The intensities of the hydrogen alpha and beta lines were obtained at predetermined frequencies for various increasing magnitudes of current flowing through the solenoid and simultaneous observations of changes in the accompanying power supplied to the oscillator, after the glow discharge had struck and thermal equilibrium had been established.

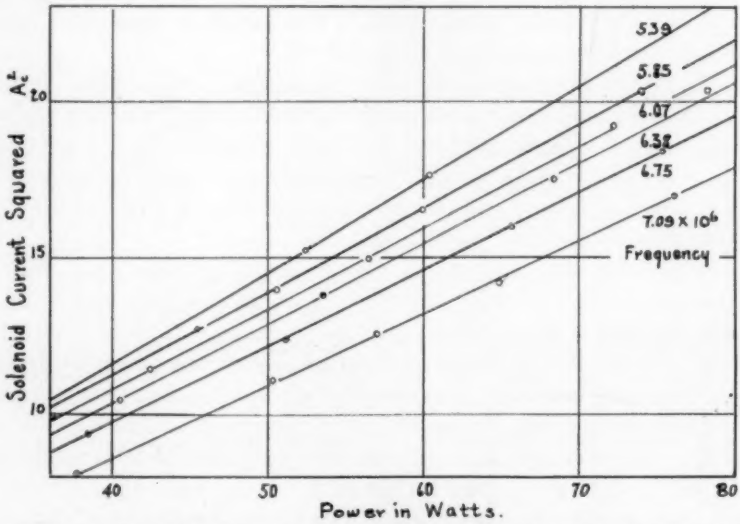
Figure 2 shows typical relations obtained between the intensity of the alpha or beta line and the current flowing through the solenoid. Figure 3 shows the accompanying linear relations existing between the square of this current and the power supplied to the oscillator.

FIG. 2.



Typical examples of relation between intensity of either α or β line at constant frequency and constant pressure but uncontrolled power supply as a function of current in solenoid or its accompanying electrical field strength.

FIG. 3.



Typical results covering same range of frequency as in Fig. 2, showing the simultaneous changes in solenoid current with accompanying power changes in the generator. Under above operating conditions, h.f. current squared in solenoid is directly proportional to the power supplied by the direct current generator.

Since in the present arrangement the current through the solenoid is proportional to the drop of potential across the coil,[5] it follows that the results shown in Fig. 2 are comparable to those obtained by Yarnold [8] from He and Ne, using a h.f. electrical field between condenser plates. His results obtained at a constant frequency of six mega-cycles, but at pressures varying from 1.0 to 20 mm. are, for low values of field strength, analogous to those shown here. Townsend [9] had shown from theoretical considerations that to a good degree of approximation, the general intensity of this type of glow discharge could be represented by the relation $Z(1 + I^2T^2)^{\frac{1}{2}} = E$, where E was the field strength, Z a force existing in the glowing gas considered as constant and independent of the current in the gas, provided the current was small, and I a quantity proportional to the intensity of the discharge if excited at frequency $1/T$. Yarnold shows that his results verify this prediction to the extent that I^2 is proportional to E for low values of field strength. Similar results are obtained for hydrogen as seen in Fig. 2.

If one expands Townsend's relation in the form of a series, omitting the higher orders, it may be reduced to $Z(1 + I^2T^2/2) = E$, or I^2/f^2 proportional to E. The result in this form may now be experimentally tested.

Unfortunately the relations expressed by the data shown in Fig. 2 are not conclusive since the field strength at any given frequency is conditioned by the power supplied by the generator. To meet this objection it is either necessary to maintain the power supply of the generator invariable, a difficult undertaking, or to proceed as follows.

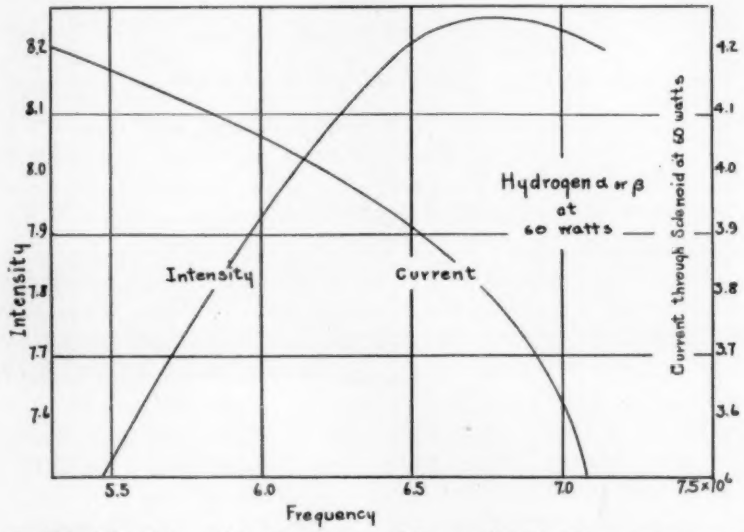
Since the data shown in Fig. 2 and 3 are obtained simultaneously it follows that the current A_e, at constant power and predetermined frequency, may be obtained by interpolation from Fig. 3. Using these current values at the given frequencies one may use Fig. 2 and from it obtain the intensity of the spectral line. The intensity as a function of frequency at constant power and the current as a function of frequency at the same constant power obtained in this way are shown in Fig. 4. From this information the intensity per unit current

[8] G. D. Yarnold, *Phil. Mag.*, **15**, 294 (1933).
[9] J. S. Townsend, *Phil. Mag.*, **13**, 745 (1932).

or the intensity per unit field strength is found to be a linear function of frequency. These final data are shown in Fig. 5.

These results seem to show, for the limited frequency range here investigated, that the relation between intensity I, fre-

FIG. 4.



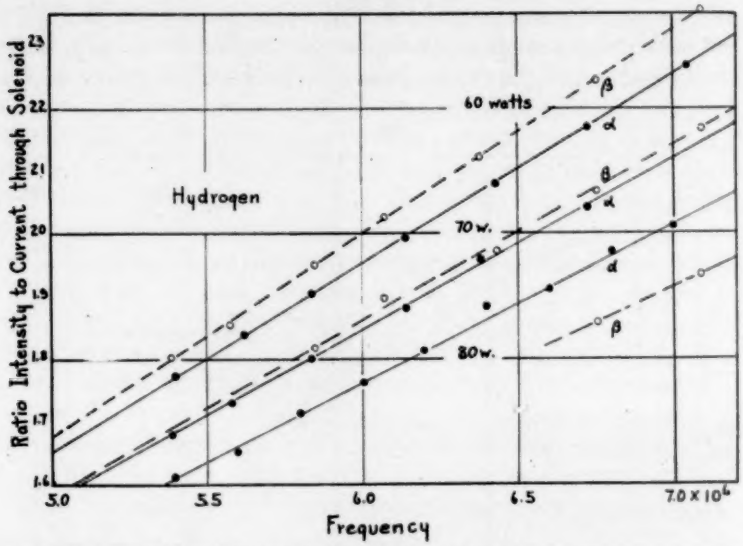
Typical relations between intensity of the α or β line as a function of frequency at constant power supply and current through solenoid as a function of frequency under analogous conditions. Results obtained from curves similar to those shown in Fig. 2 and 3.

quency f, and field strength E should be $I/f = cE$. This does not preclude the possibility that Townsend's equation may be the correct relation for a more extensive range of frequencies.

In order to meet the objection that the theoretical equation was obtained by considering the radiation from the gas as a whole we checked the relations between intensity and current, as expressed in Fig. 2, by using a photoelectric cell to measure the total intensity as Yarnold had done with He and Ne. We found under these circumstances although using different pressures but not far removed from 250 microns, because of the maximum intensity of emission near this pressure for a 2 cm. tube, that these data confirmed our original but more accurate results, examples of which are shown in Fig. 2.

It will be noticed that the intensity of both the alpha and

FIG. 5.



Showing linear relations between the intensity of the α and β lines per unit current through solenoid interpretable by using Townsend's method for measuring potential across solenoid as intensity per unit field strength as a function of frequency of the oscillating electrical field. Note relative changes in intensities of the lines with increased power supply showing impossibility of coördinating intensity changes with frequency of oscillating field unless external conditions are quantitatively interpretable. Pressure 270 microns, 2 cm. diameter tube.

the beta lines is greatest at low power input. Also at low power the beta line has greater intensity than the alpha line. On the other hand just above 70 watts the intensity of the alpha line begins to be enhanced at a greater rate than that of the beta line. At constant frequency the ratio of these intensities increases proportionally to the increase in power input. Thus at 60 volts, the ratio of I_α/I_β is 0.967; at 70 watts, 0.986, and at 80 watts, 1.05.

From this work it is concluded that the absolute values of such ratios of intensities cannot have a theoretical significance unless external conditions imposed on the gas are, as shown above, quantitatively rigidly interpretable.

We take pleasure in expressing our thanks for financial assistance rendered by the University Rockefeller Research Fund and to the National Research Council for aid in the purchase of the microphotometer.

CHAPEL HILL, N. C.
March 30, 1934.

CHEMICAL APPLICATIONS OF RECENT DIELECTRIC CONSTANT THEORY.

BY

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It now has become possible to obtain somewhat detailed information about the structure and size of molecules. Thus, structural problems have been solved due to the rapid developments in the widely divergent fields of stereochemistry and of molecular and atomic physics. It will be recalled that stereochemistry originated as an explanation of cases of isomerism and it is obvious that its methods are best suited to molecules containing an appreciable number of atoms. The methods of molecular physics, on the other hand, can be applied successfully at the present time only to very simple substances due to the theoretical difficulties of the problems involved. In the field between, where the interest lies in the relative positions and interactions of atoms and groups of atoms within molecules of intermediate complexity, the temperature variation of the dielectric constant as described by the Debye theory has found important and unique application.

There must be made another kind of differentiation when the methods used to determine the size or weight of molecules are considered. Here the classical chemical methods seem to be undergoing profound modification and change because of the introduction of newer physical theory and apparatus to give what we shall term the physical methods. It is true that both are fundamentally molecular kinetic in character and that our classification may seem at first thought to be artificial, but mention of experiments based upon the combination of (1) sedimentation velocity and diffusion theory,[1] (2) induced double refraction and diffusion theory,[2] and (3) dispersion of

[1] Svedberg, "Colloid Chemistry," Second Edition. Chemical Catalog Company, New York, 1928.

[2] Boeder, *Z. Physik*, **75**, 258 (1932); Kuhn, *Z. physik. Chem.*, **A161**, 1 (1932).

dielectric constant and Brownian movement theory,[3] suggests the advisability of such an arrangement. While one cannot claim a universal applicability for the newer physical methods it seems certain they will extend greatly our present knowledge not only of the size but also of the shape of molecules. It is of interest that these methods are of particular suitability for use in a field where the classical chemical methods have been of little avail, that of colloid chemistry. The implications of the frequency variation of the dielectric constant for this problem are all that can be properly considered in this report.

Related to these fundamental molecular problems are others to which recent dielectric constant theory may be applied. It is not our intention to attempt a complete treatment or even mention of them all, rather it will be our purpose to discuss three which are attracting much attention at the present time. The variation of the dielectric constant as a function of temperature and concentration for proper systems permits a study of molecular association and compound formation in solution to be made, thus providing a new approach to problems formerly treated making use of freezing point measurements and the Gibb's phase rule. Its quantitative aspects will be given a prominent place.

The dipole theory has also contributed in some measure to several advances which have been made in electrical engineering practice. The anomalous dispersion for radio frequencies may be of special importance in problems having to do with materials to be used for electrical insulation purposes. The attempt is made to indicate the truth of this statement, in addition there is considered the physical question which must precede it as to when molecular orientation in solids can be expected. Except in the case of certain very small molecules in which an isothermal transition from oscillation to rotation is possible, a rotation of dipole molecules in a crystalline solid has not been shown as yet to be both necessary and sufficient to account for the observed anomalous dispersion. It is possible in some substances which have been studied that the observed effects are connected with the rotational freedom of certain polar groups within the molecule, which by their elec-

[3] (*a*) Williams and Oncley, *Physics*, 3, 314 (1932); (*b*) Marinesco, *Kolloid Z.*, 58, 285 (1932); (*c*) Bloch and Errera, *Phys. Zeitschr.*, 33, 767 (1932).

tric moments contribute to the polarization when the frequency is not too high, but in general the observed variations in dielectric constant and energy absorption with frequency seem to require other explanations.

I. DIPOLE MOMENT AND MOLECULAR STRUCTURE.

No general theory has yet been elaborated which enables the properties of a molecule to be calculated from those of its constituent atoms. It is true that in some cases it is possible to carry out such a calculation but the methods used are empirical in nature. The refractivity of molecules has been studied from this point of view, using the familiar Lorenz-Lorentz equation,

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}, \qquad \text{(I-1)}$$

in which R is the molar refractivity, n is the refractive index of a monochromatic light (usually the D line), M is the molecular weight, and d is the density.

According to a number of text-books the fraction $\frac{n^2 - 1}{n^2 + 2}$ represents that fraction of the volume of a substance which is occupied by the molecules themselves, so R is the volume of N molecules or one mole of the substance, expressed in cubic centimeters. But according to the electromagnetic theory of light the charges contained in the molecule suffer definite displacements under the influence of the electrical field, so that R is more reasonably described as a measure of the electrical displacements of these charges. Indeed, Lorenz and Lorentz had called attention to a further equality in which this was recognized, namely,

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\alpha_0, \qquad \text{(I-1a)}$$

where N is the Avogadro number, and α_0 measures the deformability of the molecule.

Many years before the work of Lorenz and Lorentz an equation of similar form had been proposed by Mosotti and by Clausius, as follows:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\alpha. \qquad \text{(I-2)}$$

In this equation P is the molar polarization, ϵ is the dielectric constant, and α is a molecular constant which we shall call the "polarizability."

When these equations are investigated experimentally it is found for a number of substances that $\alpha = \alpha_0$ as the electromagnetic theory requires, yet with others α assumes values which are much larger than those of α_0, and, more striking even than that, α shows a distinct temperature variation in these cases.

The interpretation of this temperature variation we owe to Debye [4] who made the assumption that some molecules are nonpolar, while others possess finite dipole moments and are polar, in other words the product, charge times the distance between the center of gravity of positive and negative electricity within the molecule, is greater than zero. When an alternating field is applied to a system containing polar molecules there is induced in the latter an electric moment due to the displacement of charges, at the same time the dipoles which have had their moment altered in this way will tend to orient themselves in the direction of the field. This tendency is of course opposed by the thermal agitation of the molecules. This molecular rotation requires a finite time, and if the direction of the field is changing too rapidly for the response to it an orientation polarization cannot occur. The quantity α_0 is clearly the displacement or deformation polarization. For radio frequencies, on the other hand, the orientation of dipoles can take place in a gas or in an ordinary liquid, with the result that the polarization is made up of two parts, one due to deformation and the other due to orientation, both of which contribute to the dielectric constant. The magnitude of the orientation contribution depends upon the temperature of the system. Debye studied the temperature effect on the mean electric moment $\overline{m}$ of a molecule in an external field F, giving as his result the equation,

$$\overline{m} = \left(\alpha_0 + \frac{\mu^2}{3kT}\right) F. \qquad \text{(I-3)}$$

In this equation α_0 is the polarization due to deformation, μ is

[4] Debye, *Phys. Zeitschr.*, 13, 97 (1912); "Polar Molecules," Chemical Catalog Co., New York, 1929.

the permanent electric moment of the molecule, k is the Boltzmann constant, and T is the absolute temperature.

The general formula for the polarizability is, therefore,

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT}.$$

Experimental verification of this equation has followed its combination with the Clausius-Mosotti relation. This combination leads to the result,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3kT} \right) = A + \frac{B}{T}. \quad \text{(I-4)}$$

Here

$$A = \frac{4\pi}{3} N\alpha_0 \quad \text{(Molar polarization due to deformation),}$$

and

$$B = \frac{4\pi}{3} N \frac{\mu^2}{3k} \text{(Molar polarization due to orientation).}$$

This equation now enables the determination of the electric moment of a molecule from a study of the temperature variation of the dielectric constant and density. It can be applied either to a gas or vapor or to a dilute solution of polar molecules dissolved in a nonpolar solvent. In practically all the cases where gases and vapors have been studied the molar polarization P has been calculated from the data for two or more temperatures, thus making it possible to eliminate α_0 from consideration. Where dilute solutions of polar molecules in nonpolar solvents have been used it has been more common to make observations at a single temperature, evaluating α_0 in an independent manner, using optical data. The electric moment of a molecule determined in this way will be of lesser accuracy because approximations have to be made in allowing for the polarization due to the displacement of atoms.

There are molecules for which the graph of molar polarization versus reciprocal of absolute temperature does not give a straight line as required by the Debye theory and it seems important to consider the reasons in some detail. The simplest molecules in which this failure is exemplified are the ethylene

halides. Its cause was found in the rotation about the carbon to carbon bond in these molecules which was to have been expected from other observations, particularly the nonexistence of cis and trans isomers. The finite electric moment for molecules of this type is believed to represent an average of the moments of a number of molecules having effectively different dissymmetries due to the relative rotation of the two polar groups about the C—C linkage.

The first attempt at a quantitative description and solution of the intra-molecular rotation problem was made by the writer [5] who sought to calculate the effective resultant of the two equivalent doublets. This was done by assuming the position of one doublet as fixed while the projection of the other one was allowed to take up all possible positions relative to it, these positions being equally probable. The square of the mean effective moment was found to be

$$\mu^2 = \frac{1}{2\pi}\int_0^{2\pi}\left(2m \sin\theta \cos\frac{\phi}{2}\right)^2 d\phi = 2m^2 \sin^2\theta. \quad \text{(I-5)}$$

The angles θ and ϕ are made by vectors with the line joining the carbon to carbon nuclei, and with each other, respectively. Of course this equation can be applied to only those molecules for which a free and unhindered rotation can exist. Calculations of Eucken and Meyer [6] have shown that free and unhindered rotation occurs when the potential energy between the two halves of the molecule does not exceed 0.1 kT. However, if this potential energy exceeds 0.1 kT there results a rotary oscillation about the position of minimum potential energy. If the two polar vectors actually and rigidly assumed this position of minimum potential energy a zero moment for the molecule as a whole would result because in this event the vectors would take up positions transverse to each other and their effects would mutually cancel. When the rotation is hindered, or oscillatory, the amplitude of the oscillations will increase as the temperature is raised and the resultant moment of a molecule of this type will increase with the amplitude of the oscillation because the time average of the relative positions of the two polar groups will be further and

[5] Williams, *Z. physik. Chem.*, **A138**, 75 (1928).

[6] Eucken and Meyer, *Phys. Zeitschr.*, **30**, 397 (1929).

further from the trans position. This is the theoretical basis for expecting the moment of a molecule to vary with temperature and thus produce a nonlinear relation between the total polarization and the reciprocal of temperature.

It is now evident that the theoretical treatment of the case in which there is a hindered rotation requires a derivation of the relation between P, μ, and T other than that given by Debye. This has been attempted by Meyer [7] using the methods of classical mechanics. The net result of his work may be expressed by writing the new relationship in a way which will make evident the differences from the Debye equation, as follows:

$$P = \frac{4\pi}{3} N \left\{ \alpha_0 + \left[\frac{2(m \sin \theta)^2}{3kT} \right] (1 - x) \right\}. \qquad \text{(I-6)}$$

In this equation

$$x = \frac{\frac{\alpha}{kT} + \frac{\beta}{(kT)^2} + \frac{\gamma}{(kT)^3} + \cdots}{m + \frac{n}{kT} + \frac{o}{(kT)^2} + \frac{p}{(kT)^3} + \cdots},$$

and α, β, γ, m, n, o and p are constants associated with the structure of the molecule.

Thus, equation (I-6) expresses the nonlinear relationship between P and $1/T$ for the case of hindered rotation in the ethylene halides. Meyer pointed out that at high temperatures the term x becomes negligible and we have

$$P = \frac{4\pi}{3} N \left\{ \alpha_0 + \left[\frac{2(m \sin \theta)^2}{3kT} \right] \right\}. \qquad \text{(I-7)}$$

Comparison of equation (I-7) with equation (I-4) shows

$$\mu^2 = 2m^2 \sin^2 \theta,$$

which is the equation for free rotation about the linkage. Such a result would naturally have been predicted.

More recent wave mechanical treatments of the same problem have led to essentially the result of the classical

[7] Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).

mechanical analysis. Among them may be mentioned the work of Smyth, Dornte and Wilson,[8] and of Sturtevant.[9]

In some cases, at least, the newer methods result in simplified numerical computations. Furthermore, they appear to offer more direct means of attack when more complicated molecular systems are considered.

The numerical evaluation of the electric moment of a molecule in which there is hindered rotation is a somewhat complicated task. Most investigators have continued to use the methods based upon the linear equation of Debye in spite of the fact that the nonlinearity of the polarization-reciprocal of temperature relationship is clearly recognized. Greene and Williams[10] have sought to improve this situation by expanding the function x of equation (I-6), with the result that the polarization can be expressed as a function of the temperature in the form:

$$P = A + B'\left[\frac{1}{T} - C\left(\frac{1}{T}\right)^2 - D\left(\frac{1}{T}\right)^3 - \cdots\right]. \quad \text{(I-8)}$$

In this equation,

$$A = \frac{4\pi}{3} N\alpha_0,$$

and

$$B = \frac{4\pi}{3} N \cdot \frac{2(m \sin\theta)^2}{3kT}.$$

Making use of the second order term a parabolic relation between P and $1/T$ is obtained which, with proper and reasonable choice of constants, can represent the experimental data for these systems exceedingly well. In addition the theoretical ideas presented have permitted the calculation of the characteristic moments of individual linkages from the experimental data.

The most common use which has been made of electric moment data has been to determine in what configuration the constituent atoms are grouped to form the molecule. It should be emphasized that these data alone do not enable one to determine the exact dimensions and geometry of the mole-

[8] Smyth, Dornte and Wilson, *J. Amer. Chem. Soc.*, **53**, 4242 (1931).

[9] Sturtevant, ibid., **55**, 4478 (1933).

[10] Greene and Williams, *Phys. Rev.*, **42**, 119 (1932).

cule, they simply indicate whether or not the atoms are arranged in a symmetrical way. Typical examples of nonpolar or electrically symmetrical molecules are carbon dioxide, carbon bisulfide, carbon tetrachloride, methane, ethane, benzene, cyclohexane, diphenyl and dioxane. These molecules all contain polar linkages. The reason why they are nonpolar is the symmetrical arrangement of the atoms in the molecule.

Certain molecules have electric moments which may be either zero, or very small, but finite, with further experimental work necessary before final decision can be made. Prominent among them may be mentioned nitrous oxide and nitrogen tetroxide. Both Ghosh, Mahanti and Mukherjee [11] and Schwingel and Williams [12] have found values for the electric moment of N_2O which do not differ greatly from zero, suggesting a collinear arrangement of its atoms.* The results of other physical studies [13] have been interpreted to indicate the unsymmetrical linear arrangement, but there has always been difficulty in accounting for the extremely small or zero electric moment with this model, and there still may be some uncertainty. The case of nitrogen tetroxide is very interesting, if unsettled. Zahn [14] has recently published the results of work done in the vapor phase, in which the conclusion is very definite that the moment for NO_2 is smaller than that for N_2O_4, both being finite. In unpublished work of Fogelberg [15] it was concluded that the N_2O_4 molecule had the smaller moment. The data also indicated an electric moment for NO_2 which differs somewhat from the Zahn value. These data and results were never published because the dielectric constant measurements were made in carbon tetrachloride solution at a single temperature and had not been confirmed at other temperatures, in other solvents, and in the vapor phase. It is the opinion of the writer, however, that the moment for N_2O_4 should be small but not zero and we hope to be able to

[11] Ghosh, Mahanti and Mukherjee, *Zeits. f. Physik.*, **58**, 200 (1929).

[12] Schwingel and Williams, *Phys. Rev.*, **35**, 855 (1930).

* Note added in proof: In a recent article Watson, Rao and Ramaswamy (Proc. Roy. Soc, *A143*, 558 (1934)) report $\mu = 0.17 \times 10^{-18}$ e.s.u. for N_2O. This work proves the existence of a finite moment for this molecule.

[13] Plyler and Barker, *Phys. Rev.*, **38**, 1827 (1931).

[14] Zahn, *Phys. Zeitschr.*, **34**, 461 (1933).

[15] Fogelberg, Ph.D. Thesis, University of Wisconsin, 1931.

demonstrate it in the near future with experiments which are now being made.

It has been found convenient to consider the simpler polar molecules of organic chemistry as derivates of methane, benzene, water and ammonia. The electric moment data for the compounds CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are discussed in many places in the literature. The CH_4 and CCl_4 molecules have zero moments and are symmetrical. The necessary symmetry is secured by supposing the four hydrogen or four chlorine atoms to be located at the corners of a regular tetrahedron with the carbon atom at its center. One has to be careful not to expect that every molecule of the type C α_4 will have zero moment; further, care must be exercised not to conclude just because a finite moment is observed that the tetrahedral arrangement of the C-α linkages is impossible. A pyramidal model analogous to that assumed for ammonia has sometimes been suggested,[16] but it seems to have no foundation in fact. It is always found that molecules of this type are nonpolar when α is an atom, but when α is a complicated radical containing an atom like oxygen or nitrogen polar molecules probably always result. The most plausible explanation for the existence of a finite moment in these cases is that the axis of the electric moment of α need not coincide with its axis of valency if α contains such atoms as these in the group. If the directions of the valences are assumed to coincide with the axes of symmetry the finite moment can be accounted for in the following way: Since only single bonds are involved the dipole axes are free to rotate around the valence axes without change of angle, just as in the case of the rotation about the C—C bond in the ethylene halides. Again the dipole axes tend to set themselves in the position of minimum total energy, but in view of the mutual interaction between the various dipoles the four effective dipole axes are not arranged with sufficient symmetry to compensate mutually one another. The molecules $C(OCH_3)_4$, $C(OC_2H_5)_4$, $C(COOCH_3)_4$ and $C(COOC_2H_5)_4$ are polar, while $C(CH_2Br)_4$, $C(CH_2Cl)_4$ and $C(NO_2)_4$ are nonpolar.

The geometry of molecules obtained by the substitutions

[16] (*a*) Weissenberg, *Phys. Zeitschr.*, **28**, 829 (1927); (*b*) Henri, *Chem. Rev.*, 4, 189 (1927).

of atoms or groups of atoms into the benzene ring has been quite thoroughly investigated. Benzene itself is nonpolar as would be expected from the coplanar hexagonal model now widely accepted by chemists. The substitution of any single atom or group must necessarily lead to the formation of a polar molecule. The di-substituted benzenes may be either polar or nonpolar. If they have the form $C_6H_4\ \alpha_2$ the ortho and meta compounds will be polar, but the para derivatives may be nonpolar in the limited number of cases where α is an atom or one of certain types of simple groups. If the substituent groups are more complicated, and especially if they contain oxygen and nitrogen atoms, even the para disubstituted compounds may be polar. (*p*-dinitrobenzene is nonpolar.) Thus Williams [17] found that *p*-hydroquinone diethyl ether and *p*-hydroquinone diacetate have electric moments of the very appreciable magnitude, 1.7×10^{-18} and 2.2×10^{-18} e.s.u., respectively. The explanation of this fact is similar to that which has been given for the polarity of certain molecules of the type C α_4. In this case the dipole axes of the groups do not fall in the plane of the benzene ring.

Many attempts have been made to develop a quantitative vector theory for any of the disubstituted benzenes, and something has been achieved in this direction. They are usually based upon equations of Thomson [18] which can be written in the composite form,

$$\mu = [M^2 + M'^2 + 2MM' \cos\theta]^{\frac{1}{2}}, \qquad \text{(I-9)}$$

where M is the moment due to the C-α linkage acting in the plane of the benzene ring, M' is the moment due to the C-α' linkage, again acting in the plane of the benzene ring, and θ is the angle between the two dipoles. The angle θ has the values 60°, 120°, and 180° for the ortho, meta and para positions, respectively. It must be also assumed that the two dipoles do not distort one another. Although the equation has approximate validity the agreement between calculated and observed values leaves something to be desired. The deviations are particularly large in the case of the ortho compounds. The earlier investigators explained this by assuming the angle

[17] Williams, *Phys. Zeitschr.*, **29**, 271 (1928).

[18] Thomson, *Phil. Mag.*, **46**, 513 (1923).

between vectors to have been increased from 60° to something over 80°, justifying the increase by a supposed mutual repulsion of dipoles. A much more probable explanation for the lack of agreement between theory and experiment is the mutual, induced polarization created by the forces between the different parts of the molecule. This induced polarization has been discussed by Smallwood and Herzfeld [19] in a very interesting and important paper.

We wish to be very careful to point out that equation (I-9) can be of comparatively little practical use because the vectors characteristic of the polar groups usually will not be located *in* the plane of the benzene ring. As mentioned above, groups containing oxygen, nitrogen, and many other atoms will not have their electric moments in this plane. In the case of these inclined groups the geometrical addition of the dipole moments of the various radicals to obtain the resultant moment for the entire molecule must be made in three dimensions rather than in two, making the problem much more difficult of solution. There is no longer uncertainty of the *existence* of these angles of less than 180° between the directions of the dipole axis and the plane of the benzene ring, but the question of their *magnitude* is a more difficult one. Dipole moment data alone seem hardly sufficient to allow their exact determination because of the mutual induction effects between parts of the molecule which cannot always be calculated with the desired degree of accuracy. The question of the magnitude of these angles for atoms like carbon, oxygen and nitrogen in the simpler molecules probably can be best investigated by direct observation of the distances between other atoms attached to those which are not immediately adjacent using the X-ray interference method recently described by Debye and his associates.[20]

A number of workers, both in this country and abroad, have made calculations of the carbon, oxygen, nitrogen and sulfur valence angles using dipole moment data for compounds in which the dipole axes being considered are removed from one another by the interposition of hydrocarbon residues

[19] Smallwood and Herzfeld, *J. Am. Chem. Soc.*, **52**, 2654 (1930).

[20] (*a*) Debye, Bewilogua and Ehrhardt, *Phys. Zeitschr.*, **30**, 84 (1929); (*b*) Debye, ibid., **31**, 419 (1930); (*c*) Bewilogua, ibid., **32**, 265 (1931).

so that the mutual induction between individual dipoles will be reduced very greatly. Thus Smyth and Walls [21] have calculated the carbon valence angles to be inclined at 114° to one another while the oxygen valence angles are calculated to be 121 ± 5° in the diphenyl ethers and from 65 to 140° in various heterocyclic compounds. Eucken and Meyer [6] have made an interesting proposal for the decomposition of the total moments of large groups into separate components. This treatment is based upon the fact that each single substituent, or better, each linkage does have approximately a characteristic dipole moment and upon assumptions regarding the angles made by these individual group moments with each other.

Electric moment data have given valuable information with regard to the structure of such fundamental units of organic chemistry as benzene, naphthalene and diphenyl. It is found that 1,3,5-trimethylbenzene, 1,3,5-triethylbenzene, 1,3,5-trichlorobenzene and 1,3,5-tribromobenzene all have zero moments. This can be possible only if the six carbon atoms are symmetrically placed in a single plane, thus eliminating structural formulæ of the types proposed by Körner, by Baeyer and by Ladenburg. Any model in which alternate carbon atoms are in different planes must be rejected on the ground that every symmetrical trisubstituted benzene would have a finite moment in this event. The problem in the case of naphthalene is to determine whether the two rings are extended or folded. While there may be chemical evidence which has been interpreted to indicate that the 2,6 and 2,7 positions are closer than the ordinary plane formula would appear to indicate, the physical data distinctly require an extended and plane formula. The most important fact leading to this conclusion is the absence of a finite electric moment in the case of 2,6-dichloronaphthalene. Any other configuration would require a moment other than zero.

In the case of diphenyl the electric moment studies which have been made with the *p,p'* like disubstituted derivatives again require an extended arrangement of the two benzene

[21] Smyth and Walls, *Jr. Amer. Chem. Soc.*, **54**, 1854, 3230 (1932); see also Hampson and Sutton, *Proc. Roy. Soc. London*, **A140**, 562 (1933), who have given a discussion of the methods for the determination of the angles between covalencies using dipole moment data.

nuclei. All of these compounds do not have zero moments, that is not necessary. Thus *pp'* diphenol diethyl ether, *pp'* diphenol diacetate and benzidine all have finite moments, but in these substances an oxygen or nitrogen atom is joined to the hydrocarbon ring structures and we have again to consider the inclination of the axes of the electric moments to the direction of the valence linkages. Studies of the *o,o'* and *m,m'* compounds have been made in order to study the rotation of the rings themselves about the main axis of symmetry of these molecules.

Dielectric constant and electric moment studies have proven to be of some assistance in the study of isomerism. For example they have been very effective in the differentiation of the cis and trans isomers of substituted ethylenes and cyclohexanes. The classical example of this differentiation is found in the work of Errera [22] with the isomers of dichloroethylene in which the cis form is found to have a moment, $\mu = 1.9 \times 10^{-18}$ e.s.u. and the trans form is nonpolar, in accordance with the geometrical models adopted for them by organic chemists. The spatial arrangement of the hexachlorobenzenes has been discussed by Hassel and Naeshagen [23] and by Williams and Fogelberg.[24] It can be expected that dipole moment data may also contribute to the study of the configuration of isomeric derivatives of anthracene, phenanthrene, and other hydrocarbons.

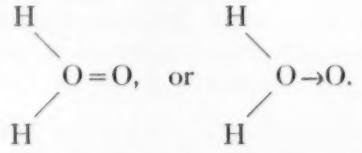
Little mention has been made of the application of these methods to compounds of inorganic chemistry. In this field of chemistry the data are comparatively few because of experimental difficulties, yet some important information has been obtained. Configurations have been assigned to the water and ammonia molecules, largely as a result of the application of other physical methods, to be sure, but the electric moment data have contributed to some extent. The investigation of compounds of arsenic, antimony, tin and silicon has been begun. Mention has been already made of work with the oxides of nitrogen.

The molecules involved have usually been of what may

[22] Errera, *Phys. Zeitschr.*, **27**, 769 (1926).
[23] Hassel and Naeshagen, *Tidskr. Kjemi og Bergvaesen*, **10**, 126 (1930).
[24] Williams and Fogelberg, *J. Amer. Chem. Soc.*, **53**, 2096 (1931).

be termed the rigid type, but this assumption does not seem possible in the hydrogen peroxide molecule. It will be remembered that in the water molecule the hydrogens are attached to the oxygen in such a way that the valence angle is much less than 180°, probably about 110°. For hydrogen peroxide two types of configuration, as indicated below, have been considered possible.

(I) H−O−O−H

(II) 

Both Smyth [25] and Linton and Maass [26] have attempted to eliminate one of them on the basis of the observation of the latter that the electric moment of hydrogen peroxide is of the order of 2×10^{-18} e.s.u. It is concluded by each that this moment seems too large to be consistent with an apparently symmetrical formula of the first type and that a formula of the second type in which both hydrogens are attached to one of the oxygen atoms is much the more probable. Actually the situation appears to be exactly the reverse, with formula I definitely the more probable one, for in all probability we are dealing not with a rigid system but with a molecule like one of the ethylene halides in which there is a rotation of polar groups, this time about the O−O linkage. This becomes evident if we apply equation (I–5) to calculate the moment a molecule of this configuration would have, provided a free and unhindered rotation could be assumed. Eucken and Meyer give 1.6 as the dipole moment of the linkage O−H, thus the calculated moment would be of the order of 2.1×10^{-18} e.s.u. assuming the oxygen valence angle to be 110°. This is a value not greatly different from the experimentally observed one. This has also been pointed out by Theilacker,[27] who has considered the several possibilities in some detail.

[25] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931.

[26] Linton and Maass, *Can. J. Research*, **7**, 81 (1932).

[27] Theilacker, *Z. physik. Chem.*, **B20**, 142 (1933).

There are many more molecules, largely organic in nature, whose electric moment data might be considered and shown to lead to interesting information about their structures but their discussion would involve more space than can be spared in this report. Finally, it seems appropriate in bringing this section to a close to remark that while considerable has been accomplished there still remains much in both theory and experiment to be improved before a quite general application of dipole moment data to structural problems can be achieved. In our discussion we have chosen to emphasize the rotation of groups within molecules because of a belief that important developments with regard to it will be forthcoming.

II. MOLECULAR ASSOCIATION AND COMPOUND FORMATION IN SOLUTION.

It is well known that liquids can be classified into two groups, usually designated by the terms associated and non-associated. Those of the former group show many abnormalities in their physical properties, supposedly due to the formation of aggregates of simple molecules to give an easily dissociated complex. The associated liquids show abnormal behavior as regards surface tension and have high latent heats of vaporization and high dielectric constants. With the exception of the lower organic acids, very little indication of this association is found in the vapor state but these compounds give abnormally high molecular weights in solution, in which form we shall be mainly concerned with them.

There have been numerous methods proposed by which it has been believed to be possible to calculate the quantitative degree of association, but it has always been a serious difficulty that the results obtained by the different methods, depending upon the abnormal properties listed above, have not always agreed with one another. The dielectric constant of a liquid does not seem to be of much use, because, while the typically associated liquids have high dielectric constants, so do other liquids which, in some quarters at least, are considered to be nonassociated. Nitrobenzene is an excellent example of such a liquid. Since the dipole moment of the molecules of a liquid does not of itself determine the dielectric constant of the liquid, it was hoped that this quantity would serve some useful purpose, but it appears that while nonpolar liquids behave

normally and are nonassociated, not all polar liquids are necessarily associated, in the chemical sense.

In recent years, attention has been turned to the study of the behavior of dilute solutions of those liquids which are known to associate in nonpolar solvents. According to the physical theory, association depends upon a mutual electrostatic interaction of the dipole molecules, and is to be considered as a condition intermediate between indifference and true chemical combination. The cause of this intermolecular action resides in the stray electrical force fields associated with unsaturated valences in the molecules, in the forces due to the molecular dipoles which vary inversely as the fourth power of the distances from the dipole centers, and in the van der Waals forces. Of these, the forces due to the molecular dipoles are the most important. A quantitative theoretical description of molecular association still seems to be far removed from us because the mutual effect of molecules upon one another depends upon several factors about which we have but scanty information. To mention but two of these factors, we do not have accurate knowledge of the location of the dipole moment, or moments, in the molecule, and we cannot describe the geometrical shape of the molecule.

It is interesting that the effects of this association become evident in the experimental study of the dielectric constants of the binary mixtures from which the electric moments of the various solute molecules are calculated. It will be recalled that in this calculation the molar polarization of the solute molecule is determined by extrapolation, to a concentration which corresponds to infinite dilution, of the curves obtained when the molar polarization of the solute molecule is plotted against the mol fraction of the solute in the solution. This extrapolation has to be made in order to avoid any effect due to the association of the solute molecules. A number of investigators have sought to make use of these curves by using the ratio $\frac{P_{M_\infty}}{P_M}$, or something equivalent, as a quantitative measure of association. In this ratio, P_{M_∞} is the extrapolated value of the molar polarization of the solute molecule referred to above, and P_M is the molar polarization of the solute molecule at any finite concentration. In the argument, the

variation of polarization with concentration is attributed to the pairing of molecular dipoles, with the value zero arbitrarily assigned to the resultant dipole moment of the two associating molecules. There is certainly no justification for such an assignment of moment, it is contrary to what may be reasonably expected when the lack of information with regard to the location of the dipoles and the irregular shape of polar molecules in general is considered. Thus, a number of articles dealing with the subject have considered the behavior of substances like formic acid and acetic acid in solution, but the conclusions must be considered as unsatisfactory because the single solute molecules have been assumed to form a symmetrical and nonpolar double molecule. A rotation of group moments within these single molecules undoubtedly exists, and its effect, combined with that of their irregular shapes, can be expected to give the double associate a finite dipole moment. In certain simpler molecules, the arrangement of the dipoles in the associate may be such as to cause mutual cancellation, with zero moment resulting.

In a recent article, Malsch [28] has discussed the effect of temperature and of the strength and frequency of the applied field on the dielectric constants of such strongly associated liquids as water and ethyl, propyl, and butyl alcohols, making use of data already existant in the literature. It is concluded (1) that the decrease of dielectric constant with field strength varies with the degree of association in such a way that the expected decrease becomes smaller the higher the degree of dissociation, and (2) the region of the anomalous dispersion, discussed in the next section, is displaced the more toward the shorter wave-lengths the more strongly the liquid is associated. These two effects are shown to be the direct result of dipole association and enable a semi-quantitative description of it. He has also considered the effect of solvent in the study of dipole association in solution, pointing out very clearly the differences which have been observed in the polarization curves for ethyl alcohol as a function of the concentration in the solvents heptane, hexane, benzene, and carbon tetrachloride. The influence of the solvent is apparently the greatest in the dilute solutions, but here the experimental difficulties are also

[28] Malsch, *Phys. Zeitschr.*, 33, 381 (1932).

greatest and the larger differences may be more apparent than real.

Closely related to the association problem is another of very great chemical significance, that of polymerization and compound formation in solution. It may be reasoned that if two substances which will combine to form a compound are dissolved together in a nonpolar solvent, the molar polarization of a new compound formed will usually differ by a considerable amount from the weighted average of the molar polarizations of the two components, the latter having been determined separately. The first publication dealing with a problem of this sort we believe to be a short note of Ebert [29] in which it was shown that when ethyl alcohol and hydrogen chloride are mixed in a nonpolar solvent the molar polarization calculated for the mixture is considerably higher than that of the sum of the individual polarizations. As far as we are aware, Ebert has never continued his work, but in very recent years several investigators have busied themselves with related problems. Thus, Hassel and Uhl,[30] whose work has different intent from that which is under consideration here, but which at the same time indicates its feasibility, have studied the mutual behavior of two kinds of polar molecules in benzene solution. Their article is concluded with the following statements: "At the beginning of this work, it was considered by all means probable that studies with mixtures of two dipole molecules in benzene solution would give definite indication of a mutual association of the two kinds of molecules. As is evident from the tables, this result has been realized only to a limited extent. To be sure, the effect is very evident in the case of chloroform and ether, but one could hardly expect anything else according to measurements of Philip (*Z. physik. Chem.*, **24**, 29 (1897)). The effect must be at least very small in the case of the *m*-dinitrobenzene and aniline system, where a molecular complex is known. The results indicate definitely that association between dipole molecules of different kind exists only to a limited extent in dilute solutions. A mutual deformation which influences the total polarization seems also not to be involved."

[29] Ebert, *Naturwiss.*, 13, 681 (1925).

[30] Hassel and Uhl, *Z. physik. Chem.*, **B8**, 187 (1930).

In work of this laboratory extending over a period of more than four years, my collaborators and I have been engaged in a theoretical and experimental treatment of the problem of compound formation in solutions. It has been reasoned that if polarization data for solutions of each of the polar components alone and of their mixtures are made available it should be possible to calculate the equilibrium constant for the combination in dilute solution. Thus, the reaction involved may be represented as follows:

$$A + B \rightleftharpoons C.$$

Considerable progress has been made using both analytical and graphical methods in the evaluation of the experimental data, but some difficulties remain. Since the graphical method used by the writer is essentially equivalent to an analytical solution worked out by Oncley we shall be content to outline the latter.

To begin with, several relationships between the mol fractions of the several constituents before and after reaction may be derived. The results of this derivation are given here:

$$\begin{aligned} \frac{f_a}{1 + f_c} &= f_2 - \frac{f_c}{1 + f_c}, \\ \frac{f_b}{1 + f_a} &= f_3 - \frac{f_c}{1 + f_c}, \\ \frac{f_s}{1 + f_c} &= f_1. \end{aligned} \qquad \text{(II-1)}$$

In these equalities, f_1 is the mol fraction of solvent before reaction, f_2 is the mol fraction of molecule A before reaction, f_3 is the mol fraction of molecule B before reaction, f_s is the mol fraction of solvent after reaction, f_a is the mol fraction of molecule A after reaction, f_b is the mol fraction of molecule B after reaction, and f_c is the mol fraction of molecule C after reaction. Further

$$\begin{aligned} P_T = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_a M_a + f_b M_b + f_c(M_a + M_b) + f_s M_s}{d} \\ = f_a P_a + f_b P_b + f_c P_c + f_s P_s \end{aligned} \qquad \text{(II-2a)}$$

and

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_2 M_a + f_3 M_b + f_1 M_s}{d}$$

$$= P_T \left(\frac{f_2 M_a + f_3 M_b + f_1 M_s}{(f_a + f_c) M_a + (f_b + f_c) M_b + f_s M_s} \right)$$

$$= P_T \cdot \frac{1}{1 + f_c} \cdot \quad \text{(II-2b)}$$

Here P_T is the total polarization of the solution after reaction, P_M is the total polarization of the system before reaction, and d is the density of the solution. Since,

$$P_M = \frac{f_a}{1 + f_c} P_a + \frac{f_b}{1 + f_c} P_b + \frac{f_c}{1 + f_c} P_c + \frac{f_s}{1 + f_c} P_s,$$

there follows from equations (II-1):

$$P_M - f_2 P_a - f_3 P_b - f_1 P_s = \frac{f_c}{1 + f_c} (P_c - P_a - P_b)$$

$$= \frac{f_c}{1 + f_c} \beta = f_3 \left[\frac{P_M - f_1 P_s - f_2 P_a}{f_3} - P_b \right]$$

$$= f_3 (\vartheta - P_b). \quad \text{(II-3)}$$

By definition of an equilibrium constant, with the concentrations expressed in mol fractions, we have

$$K = \frac{f_c}{f_a \cdot f_b} = \frac{f_c}{[f_2(1 + f_c) - f_c][f_3(1 + f_c) - f_c]}$$

$$= \frac{f_c}{(1 + f_c)^2 \left[f_2 - \frac{f_c}{1 + f_c} \right] \left[f_3 - \frac{f_c}{1 + f_c} \right]}.$$

From this equation we write

$$\frac{f_c}{1 + f_c} \cdot \frac{1}{K} = (1 + f_c) \left(f_2 - \frac{f_c}{1 + f_c} \right) \left(f_3 - \frac{f_c}{1 + f_c} \right). \quad \text{(II-4)}$$

The combination of equations (II-3) and (II-4) leads to the

important result:

$$\frac{f_3(\vartheta - P_b)}{\beta \cdot K}\left(1 - f_3\frac{\vartheta - P_b}{\beta}\right) = \left(f_2 - f_3\frac{\vartheta - P_b}{\beta}\right)\left(f_3 - f_3\frac{\vartheta - P_b}{\beta}\right). \quad \text{(II-5)}$$

If the experimental work is carried out so that the solution is extremely dilute with respect to one of the polar solute molecules, in this example, molecule B, then $f_3 \doteq 0$, and

$$-\frac{\vartheta_0 - P_b}{\beta}(Kf_2 + 1) + Kf_2 = 0.$$

If the product $Kf_2 >> 1$, the quantity β does not involve f_2 and K, and

$$\vartheta_0 - P_b = \beta = P_c - P_a - P_b. \quad \text{(II-6)}$$

Thus

$$P_c = \vartheta_0 + P_a.$$

In this important equation, P_c is the molar polarization of the compound formed in the solution, P_a is the molar polarization of the constituent A, and $\vartheta_0 = \beta + P_b$. Thus, if the quantity β can be determined the numerical evaluation of K may be achieved, since

$$K = \frac{\frac{f_c}{1 + f_c}}{(1 + f_c)^2\left(f_2 - \frac{f_c}{1 + f_c}\right)\left(f_3 - \frac{f_c}{1 + f_c}\right)}$$

$$= \frac{\frac{p}{\beta}}{\frac{\beta}{\beta - p}\left(f_2 - \frac{p}{\beta}\right)\left(f_3 - \frac{p}{\beta}\right)}$$

$$= \frac{p(\beta - p)}{f_2 f_3\left(\beta - \frac{p}{f_2}\right)\left(\beta - \frac{p}{f_3}\right)}$$

$$= \frac{p}{\xi} \cdot \frac{(\beta - p)}{(\beta - \Gamma_2)(\beta - \Gamma_3)}. \quad \text{(II-7)}$$

In these equations,

$$\xi = f_2 \cdot f_3; \qquad \Gamma_2 = \frac{p}{f_2} = \frac{P_M - f_1P_s - f_3P_b}{f_2} - P_a;$$

$$\Gamma_3 = \frac{p}{f_3} = \frac{P_M - f_1P_s - f_2P_a}{f_3} - P_b;$$

$$p = P_M - f_1P_s - f_2P_a - f_3P_b = \frac{f_c}{1 + f_c} \cdot \beta.$$

Unfortunately, the evaluation of β involves some uncertainty and inaccuracy at the present time. It should follow either by analytical or graphical methods. In the analytical method equation (II-7) is applicable. On rearrangement it becomes,

$$(\beta - \Gamma_2)(\beta - \Gamma_3) = \frac{p}{\xi} \cdot \frac{(\beta - p)}{K}.$$

It will be noted that p is a small quantity compared to β, so as an approximation $(\beta - p)$ may be replaced by β alone. Now if experiments having approximately the same p/ξ values are chosen, the corresponding values of $(\beta - \Gamma_2)(\beta - \Gamma_3)$ may be equated and β evaluated, as follows:

$$(\beta - \Gamma_2')(\beta - \Gamma_3') = (\beta - \Gamma_2'')(\beta - \Gamma_3'')$$

and

$$\beta = \frac{\Gamma_2'\Gamma_3' - \Gamma_2''\Gamma_3''}{(\Gamma_2' + \Gamma_3') - (\Gamma_2'' + \Gamma_3'')}. \qquad \text{(II-8)}$$

In the graphical method it is assumed that if components A and B react in solution to form a molecular complex the extent of the reaction will depend upon both the absolute and relative concentrations of these two components. If it were possible to obtain dielectric constant and density data for solutions which are made extremely dilute with respect to component B but which contain appreciable and sensibly constant amounts of component A it could be assumed that there were vanishingly small numbers of unreacted B molecules present at equilibrium. In that event, there would be involved solutions of the molecular complex in a solvent which contains some polar molecules of kind A, but not enough to influence seriously the result of an extrapolation of

the apparent molar polarization of the complex as a function of its concentration. By our assumption, the concentration of the complex in solution would be measured by the concentration of component B. The limiting molar polarization should then be that of the molecular complex P_c, a quantity quite simply related to β. In actual practice, it will not be possible to work with solutions which are so dilute with respect to component B that all of its molecules can be assumed to have been used up in the reaction, therefore the limiting molar polarization can be expected to be larger than P_c by an amount which approximates P_B.

The application of these methods to a specific problem will illustrate their use. Mayer has obtained dielectric constant and density data, as yet unpublished, for the ternary system; benzene, *n*-butyl alcohol and hydrogen chloride. These data are presented in the following table.

TABLE 1.

Dielectric Constant and Density Data for Ternary System C_6H_6, C_4H_9OH, HCl.

Solution.	f_1.	f_2.	f_3.	ϵ.	d.	P_M.	$f_1P_a + f_2P_a + f_3P_b$.
1.	1.0000	0.0000	0.0000	2.270	0.8733	26.581	26.581
2.	0.9563	.0286	.0150	2.551	.8729	30.162	28.451
3.	.9542	.0266	.0192	2.550	.8734	30.090	28.382
4.	.9199	.0391	.0410	2.828	.8750	32.967	29.371
5.	.9541	.0207	.0252	2.525	.8740	29.660	28.098
6.	.9649	.0133	.0218	2.448	.8741	28.711	27.620
7.	.9670	.0111	.0219	2.433	.8739	28.518	27.490
8.	.9661	.0104	.0235	2.417	.8739	28.278	27.467
9.	.9833	.0049	.0119	2.326	.8734	27.211	27.005
10.	.9741	.0050	.0209	2.360	.8733	27.541	27.117

From these data there have been determined the several quantities necessary for the calculation of the equilibrium constant K. The value of β was obtained from a graphical determination of the limiting polarization of the complex which gave $P_c = 230$. Since P_a (C_4H_9OH) = 80 and P_b (HCl) = 30, $\beta = 120$. These quantities, with the results of the calculation for K, are given in Table 2.

The value of K which is obtained in any calculation is of course greatly dependent upon the value of β used. Therefore, until values of β can be established with more certainty,

TABLE 2.

Equilibrium Data for n-Butyl Alcohol—Hydrochloric Acid Complex. $\beta = 120$.

p.	Γ_3.	Γ_4.	$\xi \times 10^4$.	$\frac{p}{\xi}$.	K.
0.000	—	—	—	—	—
1.711	59.8	103.8	4.303	3980	482
1.708	64.1	89.2	5.100	3350	230
3.596	92.0	87.6	16.027	2240	288
1.562	75.5	61.8	5.217	3000	137
1.091	82.0	50.1	2.895	3770	169
1.028	92.5	47.0	2.428	4230	250
0.811	78.1	34.6	2.440	3320	111
0.206	42.5	17.3	0.576	3580	54
0.424	84.8	21.1	1.046	4050	139

the results for K which are obtained in any calculation can only suggest a magnitude. It is also possible that the K values will not be constant but will vary with changing dielectric constant of the solution. It is our intention that the rather detailed discussion of the compound formation problem given here should serve as a report of our progress with the work, and nothing more. Data for a number of ternary systems have been obtained, and with interesting results, but much remains to be done in the way of a really quantitative interpretation.

There are important special and simpler cases of this general problem, only one of which will be treated in this report. It deals with a polymerization reaction of the type $A_2 \rightleftharpoons 2A$. A well-known system which conforms to this equation is the equilibrium mixture of nitrogen tetroxide and nitrogen dioxide dissolved in a nonpolar solvent. Since the equilibrium constant for this system is known at several temperatures, it should be a comparatively easy problem to calculate the molar polarizations of the solute molecules from dielectric constant and density data for dilute systems. This is, in a sense, the reverse of the general problem considered above where the object was to determine the equilibrium constant from the polarizations of the several solute molecules.

In the work of Fogelberg [15] referred to in the first section dielectric constant and density data were obtained for the ternary system CCl_4, N_2O_4, NO_2, at 0° C. The equilibrium

constant for the reaction can be expressed in the form,

$$K_c = \frac{C^2_{NO_2}}{C_{N_2O_4}} = \frac{4\alpha^2 C}{1 - \alpha},$$

where C_{NO_2} and $C_{N_2O_4}$ are the concentrations of NO_2 and N_2O_4, expressed in moles per liter, and α is the degree of dissociation. At low temperatures, N_2O_4 is only slightly dissociated and we can assume α to be inversely proportional to the square root of the total concentration. The molar polarization of N_2O_4 can be calculated directly from this inverse square relationship, using data for several concentrations without any knowledge of the numerical value of the dissociation constant.

If, as is indicated by our preliminary data, the electric moment for N_2O_4 should turn out to be either zero or something not greatly different from it, the electric moment of NO_2 can be readily calculated. In this event, the system consists of the polar solute NO_2 dissolved in a nonpolar solvent mixture composed of carbon tetrachloride and nitrogen tetroxide. The problem thus reduces to that of a binary mixture because the concentration of the NO_2 molecules can be obtained from the equilibrium constant data.

(To be concluded)

RECENT DEVELOPMENTS IN MOLECULAR RAYS.

BY

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Since the publication, in 1931, of two reviews [1,2] of the work in molecular rays, some important advances have been made in experimental technique, and fundamentally new results have been obtained both in experiment and in theory. It is the purpose of the present paper to bring the survey of this subject up to date. In view of the existence of the above reviews, references will be given to important recent papers only.

A molecular ray or beam consists of a stream of neutral particles, molecules or atoms, confined to a very small solid angle by a system of narrow slits, the density being so low that no collisions occur within the beam. Normally the source of the ray is an enclosure containing molecules having Maxwellian distribution of velocities, so that the particles in the ray are non-homogeneous in speed. They may be made homogeneous by various devices (by a pair of rotating toothed wheels [2,3] or vibrating slits [3] or by selection from a "velocity spectrum" produced by inhomogeneous electric or magnetic fields [4] or by diffraction from crystal surfaces [2,3]), but all such devices seriously reduce the intensity, which is frequently near the limit of quantitative measurement in the whole, non-homogeneous beam. Consequently, relatively few experiments have been performed with homogeneous beams, although this feature would be desirable in most cases.

In a molecular ray the molecules are in a uniquely simple and easily controlled state. It is not surprising, therefore, that this experimental tool has yielded information not ob-

[1] W. H. Rodebush, *Rev. Mod. Phys.*, **3**, 392 (1931).

[2] J. B. Taylor, *Ind. and Eng. Chem.*, **23**, 1228 (1931).

[3] T. Tykociner, *Phys. Rev.*, **44**, 322 (1933).

[4] Rabi and Cohen, *Phys. Rev.*, **43**, 377 (1933).

tainable at all, or as readily, by other means. Obviously, as the ray becomes more nearly homogeneous in direction and speed, its behavior will exhibit more nearly the behavior of the single particles. At the same time, since a molecular ray experiment always involves a large number of individuals, any statistical law governing their behavior will also become apparent. The Stern-Gerlach experiment on the space quantization of silver atoms in the magnetic field is a classical example showing both the individual and the statistical behavior of atoms.

TECHNIQUE.

From the very inception of molecular ray measurements, one outstanding source of difficulty was the extremely low intensity of the rays. The most sensitive means of detection was (and for some cases still is) condensation on smooth surfaces, accompanied by or followed by chemical reaction or "development." For quantitative measurements the most generally useful method has been to allow the beam to enter through a slit into an otherwise closed chamber, and to measure the resulting pressure rise in the chamber. Ellett and Zabel [5] have perfected the Pirani gauge for this purpose so that pressure changes of 5×10^{-9} mm. Hg may be measured. This amounts to one part in a thousand of easily attainable beam pressures.

Recently Estermann and Stern [6] have developed a method of measuring pressures, adaptable to all kinds of molecules, which promises to exceed all previous methods in sensitivity and reliability. The method makes use of an effect described by Kingdon.[7] The molecular ray passes through a slit into a chamber containing a hot cathode. The latter is made sufficiently negative relative to the chamber walls so that the entering molecules are ionized by the electrons coming from the cathode. The ions fall toward the cathode and normally spiral about it a great number of times before dropping into the cathode or being otherwise removed. Consequently, they have a great effect upon the space charge and upon the resulting electron current. With a relatively crude prelimi-

[5] Ellett and Zabel, *Phys. Rev.*, **37**, 1102 (1931).
[6] Estermann and Stern, *Zeits. f. Physik*, **85**, 135 (1933).
[7] K. H. Kingdon, *Phys. Rev.*, **21**, 408 (1923).

nary apparatus, pressures of mercury vapor down to 4×10^{-11} mm. were detected. This sensitivity is so great that much of it could be sacrificed to obtain very rapid response, say in 1/100 second. The authors suggest that the beam could be interrupted at low audio frequency, and the resulting A.-C. component of the electron current amplified in the usual way, thus greatly increasing the sensitivity and completely eliminating the very troublesome slow drifts of "background" pressure. The method has not yet been applied to actual experiments.

SCATTERING OF MOLECULAR RAYS IN GASES.

In the quantum mechanical theory of scattering, the motions of colliding molecules are governed by the diffraction of their associated DeBroglie waves. These wave-lengths are given by the relation: $\lambda = h/mv$ (h = Planck's constant, m = mass, v = velocity of molecules). For the lighter molecules, at room temperature, the associated waves are of the order of 10^{-8} cm., that is, of the same order as the diameters of the molecules themselves. Consequently, diffraction phenomena should become important in determining the paths of scattered molecules.

The general quantum mechanical treatment of collision phenomena has been given by Born.[8] The theory has been applied to molecules by Mitzushima [9] and by Massey and Mohr,[10] using a simple rigid sphere model for the molecules, and also a rigid sphere with an attractive field of force. These investigations show that: (1) The total scattering remains finite even if the small angle scattering down to zero angle is included, provided the attractive field drops off faster than r^{-3}. (In the classical theory, the collision radius becomes infinite at zero scattering angle.) (2) The effective scattering radius is about twice the radius of the rigid sphere molecule. (3) Collisions of *like* molecules are greatly influenced by interchange (resonance) forces.

Obviously, molecular rays afford an excellent means for investigating the details of molecular collisions and inter-

[8] M. Born, *Zeits. f. Physik*, **38**, 803 (1926).

[9] S. Mitzushima, *Phys. Zeits.*, **32**, 798 (1931).

[10] Massey and Mohr, *Proc. Roy. Soc* **A141**, 434 (1933).

molecular forces. Ellett and Zabel [11] investigated the scattering of beams of H_2 in H_2 and in air, as a function of pressure of the scattering gas. Mais and Rabi [12] scattered beams of K atoms in H_2, He, N_2 and CO_2. They found that the effective collision radii were greater than those predicted from kinetic theory or lattice distances, but did not find any marked effects of diffraction. This was not to be expected, as the most probable wave-length of the K atoms was 2×10^{-9} cm., that is, considerably smaller than the diameters of the scattering molecules.

Knauer [13] investigated the dependence on angle of scattering, between 22.5° and 124°, for the case of He, H_2, H_2O, and O_2, each in its own gas, and also for He and H_2 in mercury vapor. He found no maxima and minima in any case. Indeed, Mitzushima had predicted that the theoretical maxima would probably be obliterated by the broad range of velocities (and consequently, of DeBroglie wave-lengths) in a nonhomogeneous beam. Nevertheless, by using a greatly improved apparatus of high resolving power, Zabel [14] was able to demonstrate clearly the existence of maxima. He scattered H_2 in H_2 and He in He, making measurements from about 4° to 70° from the incident beam. For the case of He his results were in satisfactory agreement with the theoretical curves of Massey and Mohr, due allowance being made for the non-homogeneity of the beam and other experimental conditions.

Fraser and Broadway,[15] and Broadway [16] performed scattering experiments which were deliberately designed to test the theory of Massey and Mohr.[10] For this purpose it was advantageous to confine the scattering to a very short portion of the beam, so that the detecting device would include the same angle relative to all the scattered molecules. This they accomplished by a method of crossed beams, using beams of trans-di-iodo-ethylene and of mercury atoms to scatter

[11] Ellett and Zabel, *Phys. Rev.*, **37**, 1112 (1931).
[12] Mais and Rabi, *Phys. Rev.*, **43**, 378 (1933).
[13] F. Knauer, *Zeits. f. Physik*, **80**, 80 (1933).
[14] R. M. Zabel, *Phys. Rev.*, **44**, 53 (1933).
[15] Fraser and Broadway, *Proc. Roy. Soc.*, A141, 626 (1933).
[16] L. F. Broadway, *Proc. Roy. Soc.*, A141, 634 (1933).

beams of Na and K atoms. All of their results could be interpreted in terms of the quantum mechanical theory.

The predictions of this theory are most characteristic in the region of small angle scattering. For this reason Mais [17] carried out experiments on the scattering of potassium atoms in He, Ne, A, H_2, N_2 and CO_2 down to an angle of about 4.5 minutes. He found a striking predominance of scattering at small angles, as predicted by the theory. H_2 and He scatter like hard spheres, but the other gases, even Ne, seem to have attractive forces of considerable range.

DIFFRACTION OF MOLECULAR RAYS ON CRYSTAL SURFACES.

The success of Davisson and Germer in verifying the De-Broglie matter wave relation for electrons gave fresh impetus to the study of reflection of molecules on crystal surfaces. As stated above, the wave-lengths associated with molecules are usually in the X-ray region, so that rays of molecules incident on crystal surfaces should show diffraction phenomena. Such effects were sought by a large number of experimenters.[18, 19, 20] In all cases, there was considerable diffuse reflection plus some definitely directed reflection which sometimes deviated from the specular angle. An explanation of the diffuse reflection is afforded by experiments of Veszi,[21] who reflected molecular rays from oil surfaces moving rapidly at right angles to the incident rays. He showed that the molecules were adsorbed and reëvaporated 10^{-4} to 10^{-5} seconds later.

The first unambiguous demonstration that the DeBroglie relation is valid for molecules was given by Stern and his co-workers.[22] Using beams of He and H_2 reflected from LiF crystals, they obtained conclusive evidence of diffraction in four orders, as of a surface *cross* grating, the grating space being the distance between rows of *like* ions.

Estermann, Frisch, and Stern [23] achieved a more precise

[17] W. H. Mais, *Phys. Rev.*, **45**, 773 (1934).
[18] Zahl and Ellett, *Phys. Rev.*, **38**, 977 (1931).
[19] J. M. B. Kellogg, *Phys. Rev.*, **41**, 635 (1932).
[20] R. R. Hancox, *Phys. Rev.*, **42**, 864 (1932).
[21] G. Veszi, *Zeits. f. Phys. Chem.*, B11, 211 (1930).
[22] Estermann and Stern, *Zeits. f. Physik*, **61**, 95 (1930).
[23] Estermann, Frisch and Stern, *Phys. Zeits.*, **32**, 670 (1931).

verification of the DeBroglie relation by using a nearly homogeneous beam of helium molecules. This they obtained in two ways: by separating out a narrow diffracted beam from a LiF crystal, and by a pair of rotating toothed wheels.

Zener [24] has made a theoretical investigation of the reflection of molecules on a crystal lattice. For the case of H_2 reflected from LiF at room temperature, he finds that a large fraction of the molecules (about 0.9) should be reflected elastically.

Stern had also tried NaCl crystals, but the results were doubtful because of the strong diffuse reflection. Zabel,[25] however, succeeded in obtaining diffraction of He, Ne, and A on NaCl by using surfaces freshly cleaved in dry air or dry hydrogen. The observed diffraction pattern was evidently due to a surface grating formed by rows of adjacent *unlike* ions. With small amounts of moisture present, however, there was evidence of a spacing twice as great, just as Stern had found for LiF crystals.

In their most recent work, Frisch and Stern [26] have demonstrated a fundamentally new effect which promises to be very important for the development of an adequate theory of the interaction of molecules and crystal lattices. Since the DeBroglie wave-lengths, and consequently the angles of diffraction, depend upon the velocity of the molecules, one expects that the graph of diffracted intensity plotted as a function of diffraction angle should be a smooth curve corresponding to the continuous distribution of velocities in the incident beam. However, the experimental graph shows pronounced dips (Dellen) at those angles at which the components of the momentum of the reflected molecules relative to two of the crystal axes have certain discrete values, just as if these values of the momentum components were "forbidden." Similar effects are obtained when the momentum components of the *incident* molecules have these forbidden values.

All of the above diffraction experiments show that molecular rays do not penetrate the crystal lattice, but are affected by the conditions on the very surface of the crystal only.

[24] C. Zener, *Phys. Rev.*, **40**, 178 (1932).
[25] R. M. Zabel, *Phys. Rev.*, **42**, 218 (1932).
[26] Frisch and Stern, *Zeits. f. Physik*, **84**, 430 and 443 (1933).

Therefore, they afford a means of investigating the structure of surfaces, the formation of surface films, and allied phenomena. The work done in this field is, as yet, very limited, but the following references will show a few of the possible applications of this technique.

Johnson [27] diffracted hydrogen atoms from the cleaved [100] surface of LiF, and obtained evidence for the existence of the Zwicky secondary structure. Ditchburn [28] deposited Cd atoms on a target directly behind a tapering slit and studied the surface migration of the deposited atoms. Coper, Frommer and Zocher [29] studied the formation and orientation of surface layers produced by rays of metal atoms and metallic salt molecules. Johnson and Starkey [30] produced thin layers of Hg atoms mixed with controlled amounts of H_2, O_2, A, and CO_2, and studied the nature of these adsorbed films by measuring their conductivity and other properties.

MAGNETIC AND ELECTRIC MOMENTS OF ATOMS AND MOLECULES.

In atoms, permanent magnetic moments are associated with the electron spins and with the angular momentum of the electronic configuration about the nucleus (the "orbital motion" of the Bohr theory). These magnetic moments are expressed in the unit: $eh/4\pi mc$, the Bohr magneton (B.M.). In addition, there may be, in some cases, a magnetic moment associated with the nucleus, which is presumably of the order of 1/1840 B.M., a unit which has been called the nuclear magneton (N.M.). In molecules, there may be still another magnetic moment due to rotation of the molecule as a whole. All these magnetic moments are, of course, associated with mechanical angular momenta, and it is the magnitudes of the latter, and their coupling relations, which determine the number of possible quantized orientations in a magnetic field. When a beam of atoms or molecules is passed through a non-homogeneous magnetic field (Stern-Gerlach experiment) it is split up into a number of discrete beams depending upon the number of possible orientations. Thus the *number* of beams

[27] T. H. Johnson, JOUR. FRANK. INST., **212**, 507 (1931).
[28] R. W. Ditchburn, *Proc. Camb. Phil. Soc.*, **29**, 131 (1933).
[29] Coper, Frommer and Zocher, *Zeits. f. Electrochem.*, **37**, 571 (1931).
[30] Johnson and Starkey, *Proc. Roy. Soc.*, A140, 126 (1933).

depends upon the *mechanical* moments, while their *separation* depends, among other factors, upon the strength of the *magnetic* moments. By noting the number of maxima in the Stern-Gerlach pattern, and the shift in their relative positions with increasing field strength, it is possible to obtain information about both mechanical and magnetic moments. The theory is outlined briefly, and specialized for the alkalies by Breit and Rabi.[31] Using an improved apparatus of high resolving power, Rabi and Cohen [32] have found the mechanical moment of the sodium nucleus to be 3 electron spin units ($\frac{1}{2} \times h/2\pi$). The magnetic moment of two alkalies, Li and K, was found by Meissner and Scheffers,[33] to be 0.916×10^{-20} gauss cm. $\pm \frac{1}{2}$ per cent. (The theoretical value of the Bohr magneton is 0.917×10^{-20} from spectroscopic data and 0.922×10^{-20} from electron deflection measurements of e/m. The best data available at present for the fundamental physical constants seem to favor the former value.[34]) For the nuclear magnetic moment these authors get either 5 per cent. or 0.5 per cent. of a Bohr magneton, depending upon the coupling conditions assumed. The precision of the method by which these nuclear moments are determined is difficult to estimate.

The case of the iron atom is of particular interest, since it had been reported by Gerlach as non-magnetic, while spectroscopic evidence predicts that it should have a permanent magnetic moment. A recent experiment by Klabunde and Phipps [35] shows definitely that a magnetic moment is present, but the resolution is not sufficient to give the numerical magnitude.

Of the molecules, O_2 was one of the first to be attacked, but it proved unexpectedly difficult to work with experimentally. In addition, the interpretation of the data is much more involved than in the case of atoms, because of the coupling of the atomic angular momenta with the angular momentum of the molecular rotation. Nevertheless, Schnurmann [36] has

[31] Breit and Rabi, *Phys. Rev.*, **38**, 2082 (1931).
[32] Rabi and Cohen, *Phys. Rev.*, **43**, 582 (1933).
[33] Meissner and Scheffers, *Phys. Zeits.*, **34**, 48 and 245 (1933).
[34] R. T. Birge, *Phys. Rev.*, **40**, 228 (1932).
[35] Klabunde and Phipps, *Phys. Rev.*, **45**, 59 (1934).
[36] R. Schnurmann, *Zeits. f. Physik*, **85**, 212 (1933).

succeeded in showing that the normal state of O_2 is the $^3\Sigma$ state, in agreement with the result obtained by Mulliken from an analysis of the band spectrum.

The magnetic moment of the hydrogen molecule has been determined by Frisch and Stern,[37] and Estermann and Stern.[38] It is of interest, of course, because of its relation to the magnetic moment of the proton. In the normal (singlet) state of H_2, the electron spins are antiparallel, and should cancel, leaving only the moments due to the nuclear spins and the rotation of the molecule. In para hydrogen the lowest rotational quantum number l is zero and the nuclear spins are opposed, while in ortho hydrogen the lowest l is one and the nuclear spins are parallel. Therefore, at sufficiently low temperatures, the former should be nonmagnetic but the latter magnetic. This is checked by experiment. Further, at higher temperatures, para hydrogen with $l = 2$ may be measured, and the rotational magnetic moment per unit of l obtained. This is found to be 0.8 to 0.9 N.M. Subtracting this from the moment observed in the ortho form, the moment of the proton is found to be 2.5 N.M. $\pm$ 10 per cent. In view of the great experimental difficulties of measuring such extremely small moments, the precision of the results is remarkable. Between the experimental observations, however, and their interpretation as nuclear moments, several assumptions intervene whose correctness is not completely certain in the present state of theory.

It is very fortunate, therefore, that Rabi * has succeeded in measuring the proton moment in hydrogen *atoms*, for in this case the deduction from the data is more direct. The experimental conditions are very exacting, however, as the proton moment must be measured in the presence of the much larger electron moment. His method depends essentially on using highly inhomogeneous yet very weak fields, so that the proton and electron spins are not wholly decoupled. The electron is then under the combined influence of two magnetic fields, the external applied field and that of the proton. The

[37] Frisch and Stern, *Zeits. f. Physik*, **85**, 4 (1933).

[38] Estermann and Stern, *Zeits. f. Physik*, **85**, 17 (1933).

* Private communication, for which the writer is greatly indebted to Professor Rabi.

observed deflections are a function of both fields, and since one is known the other may be deduced. The resulting value of the proton moment is 3 ± 0.3 N.M. A particularly elegant feature of this experiment is that the field is produced by a simple arrangement of current carrying wires in air, so that its value at any point may be calculated and reproduced precisely.

By the same methods, Rabi has found the magnetic moment of the deuton to be 0.75 ± 0.2 N.M. Stern [39] had previously found, from rough preliminary measurements, that the value for the deuton was certainly less than for the proton, about 1.5 N.M. (The *mechanical* moment (spin) of the deuton is *twice* that of the proton.[40])

Analogous to the measurement of magnetic moments is the determination of permanent electric dipole moments by sending a molecular ray through a nonhomogeneous electric field. The technique is difficult, and the interpretation of the data is complicated because of the fact that the measurable, time average, dipole moment depends not only upon the value of the intrinsic moment, but upon the field strength, orientation of the molecule, and energy of rotation. Nevertheless, the molecular ray method has certain advantages over other ways of measuring dipole moments. These are discussed in some detail by Estermann and Fraser,[41] who use the method to find the dipole moment of HCl, which they report as about 1.95×10^{-18} esu. Details of the technique are given by Estermann and Wohlwill,[42] who also give semi-quantitative results for several organic molecules. The first really good quantitative determination (for *p*-nitranilin) has been obtained by Wohlwill.[43]

SPACE QUANTIZATION.

The problem of the "double Stern-Gerlach experiment" may be stated as follows: By sending a beam of atoms through a non-homogeneous magnetic field, and separating out one of

[39] Estermann and Stern, *Zeits. f. Physik*, **86**, 132 (1933).
[40] Murphy and Johnston, *Phys. Rev.*, **46**, 95 (1934).
[41] Estermann and Fraser, *Jour. Chem. Phys.*, **1**, 390 (1933).
[42] Estermann and Wohlwill, *Zeits. f. Phys. Chem.*, B**20**, 195 (1933).
[43] M. Wohlwill, *Zeits. f. Physik*, **80**, 67 (1933).

the two resulting parts, there is obtained a beam in which the spins of all the atoms are parallel. This is now sent through a second, uniform, field whose direction is not parallel to these spins. The question is: will all the spins turn parallel to the second field, or will some of them "tip over" into an antiparallel direction? Obviously, this can be determined by passing the beam through a third, non-homogeneous field.

The occurrence of the antiparallel orientations had been predicted theoretically, but the effect had not been observed. The theory, however, made the assumption that the transition into the second field is instantaneous, whereas in the actual experiment the transition is gradual, that is, the atom experiences a gradually rotating field about itself. Güttinger [44] supplied the theory for this case, and found that to get an appreciable fraction of antiparallel atoms, the period T_f of the rotating field must be of the same order as the Larmor period T_l of the atoms. In the usual experimental arrangement $T_f \gg T_l$. Phipps and Stern [45] succeeded in devising an experiment to realize the requirement: $T_f \backsimeq T_l$ but obtained negative results. This was explained by Rosen and Zener,[46] who extended Güttinger's theory by taking account of the fact that the rotation of the field begins and ends gradually, and not abruptly as Güttinger had assumed. They found that no anti-parallel orientations should occur if the total angle turned through by the field is an integral multiple of 2π. In the experiment of Phipps and Stern this angle was just 2π. More recently, however, Frisch and Segrè [47] have actually obtained up to 35 per cent. "tipped-over" atoms, although the total angle of rotation was again 2π. However, their rotating field was produced by combining a very weak homogeneous field with the field due to a current in a single wire. At a point near the wire, the total field was zero and changed sign, and the "rotating" field at the atoms was produced by passing the beam near this point. This case (which is obviously quite different from the one considered by Rosen and Zener) has been treated theoretically by Majorana.[48]

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[44] P. Güttinger, *Zeits. f. Physik*, **73**, 169 (1931).
[45] Phipps and Stern, *Zeits. f. Physik*, **73**, 185 (1931).
[46] Rosen and Zener, *Phys. Rev.*, **40**, 502 (1932).
[47] Frisch and Segrè, *Zeits. f. Physik*, **80**, 610 (1933).
[48] E. Majorana, *Nuovo Cim.*, **9**, 43 (1932).

VARIOUS ADDITIONAL APPLICATIONS.

The following recent applications of molecular rays will indicate a few of the many types of investigations in which this technique can be used to advantage. The work of Lewis[49] on alkali vapors is an example of the application of molecular rays to problems in the kinetics of gas reactions. A beam of Na vapor is passed through a non-homogeneous magnetic field. The magnetic atoms are deflected, the molecules, being non-magnetic, are not. By thus measuring the degree of dissociation at various beam temperatures, both the heat of dissociation and the equilibrium constant may be obtained for the $Na_2 \rightleftarrows 2Na$ reaction. The method was also used for Li and K.

Ko[50] obtained similar data for bismuth vapor, using, however, an entirely different technique. With the mechanical velocity selector of Zartman,[51] he analyzed the velocity "spectrum" of a mixed beam of Bi and Bi_2 and obtained the relative abundance to within 1 per cent. This method is more generally applicable than the above since it is independent of the magnetic properties of the atoms and molecules. It is more exacting, however, with regard to resolving power.

Taylor[2] has pointed out the possibility of producing gaseous reactions entirely uninfluenced by solid surfaces (walls of the container) by means of crossed molecular beams. Conversely, by letting a beam impinge on a surface, the effect of the latter may be studied. This has been done, for beams of organic molecules and surfaces of hot platinum and tungsten, by Rice and Byck.[52]

An interesting new method of producing atomic rays of nearly homogeneous velocity has been developed by Beeck and Wayland.[53, 54] The method consists of ionizing the atoms, accelerating them in an electric field, selecting out a narrow range of velocities, neutralizing to uncharged atoms, and again selecting out a beam that is homogeneous in direction and

[49] L. C. Lewis, *Zeits. f. Physik*, **69**, 786 (1931).
[50] C. C. Ko, *Phys. Rev.*, **44**, 129 (1933).
[51] J. F. Zartman, *Phys. Rev.*, **37**, 383 (1931).
[52] Rice and Byck, *Proc. Roy. Soc.*, **A132**, 50 (1931).
[53] O. Beeck, *Ann. de Physique*, **19**, 121 (1934).
[54] Beeck and Wayland, *ibid.*, **19**, 129 (1934).

speed. Since one ion-volt corresponds to the average kinetic energy of heat motion at about 10,000° C., and since atomic rays corresponding to several hundred ion-volts are easily obtained, it follows that these rays have very much greater energy than those produced in the usual way. This technique is used to study the ionization of argon by neutral argon atoms. It is found that the ionizing efficiency of the atoms is four or more times as great as that of ions. This is in accord with the theoretical results of Stückelberg,[55] Weizel and Beeck,[56] and Zwicky.[57]

As a final example we may consider the following fundamental experiment: In 1926 Stern pointed out that molecular rays ought to make possible a direct test of the Einstein recoil of radiating atoms. The effect to be measured is, of course, extremely small, but by using very long and narrow and perfect beams, Frisch [58] was able to demonstrate that an atom does suffer a change of momentum of the predicted magnitude and direction when it absorbs or emits a photon. In one of the experiments, a beam of sodium atoms was illuminated strongly from one side by light of the Na D-lines. By the absorption and reëmission of the photons, the beam should be displaced sideways, and broadened. Both effects were observed, the shift of the beam being about 0.01 mm., as predicted.

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[55] E. C. G. Stückelberg, *Helv. Phys. Acta*, **5**, 369 (1932).
[56] Weizel and Beeck, *Zeits. f. Physik*, **76**, 250 (1932).
[57] F. Zwicky, *Proc. Nat. Acad. Sci.*, **18**, 314 (1932).
[58] R. Frisch, *Zeits. f. Physik*, **86**, 42 (1933).

Ice from the Bottom of the Sea.—(*Science Service.*) GEORGES CLAUDE, famed French inventor of the neon sign and exponent of obtaining power by using the differences in the top and bottom temperatures of the ocean, is taking a sea-going ice plant to Brazil where he plans to make fresh ice from sea water. By using half of the three thousand horsepower plant aboard ship, M. Claude expects to manufacture 1,000 tons of ice every 24 hours. A steel tube 11½ feet in diameter will be sunk to the bottom of the ocean 2,300 feet below. Water brought up the long tube will have a temperature of 41 degrees Fahrenheit.

In another part of the system surface water is led in at a temperature around 80° F. Now, if a partial vacuum is introduced until the warmer water begins to boil, the vapor or low pressure steam will flow toward the condenser surrounded by the depth water at 41° F. because the pressure is lower at this cooler point. The steam as generated passes through eight turbines on its way to the chamber of still lower vacuum. With a 39 degree difference of temperature M. Claude expects to generate his 3,000 horsepower. The condensed vapor furnishes pure, fresh water for the making of ice and is available at a temperature approximately that of the depth water.

C.

Urushiol.—(*Science Service.*) Who ever would have thought such a close relationship existed between the well-known Japanese lacquer and that great American nuisance poison ivy? After a long series of chemical manipulations, Prof. G. Albert Hill of Wesleyan University, Middletown, Conn. was able to isolate from the bark of the poison ivy plant the substance known as urushiol, first obtained by the Japanese chemist Majima from Japanese lac. The lac is obtained from a tree belonging to the sumac family, of which poison ivy is also a member. It is not surprising then that during the mah jong craze a few years ago, numerous cases of lacquer poisoning were traced to game sets imported from the Orient. Japanese makers of lacquered work seem to have acquired over a period of years an immunity toward the poisonous action of urushiol.

C.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

SAFETY IN MARINE TRANSPORTATION.

The Bureau's activities having a bearing on safety requirements for ship construction, equipment, cargo, and stowage, and on aids to navigation, have included a considerable range of subjects, some of which are briefly indicated below. Further items thereon will be given in succeeding issues. The projects or tests were undertaken mainly at the request or with the coöperation of the Bureau of Navigation and Steamboat Inspection, the Bureau of Lighthouses, the United States Shipping Board, and groups of marine underwriters.

Fire Resistance in Ship Construction.—The use of steel in hulls, decks, and bulkheads, while effecting a decided increase in safety compared with wood construction, would not as such be expected to prevent the occurrence of disastrous fires to any greater extent than incombustible walls, partitions, columns, and floors in buildings. In both cases the spread of fires in combustible furnishings, trim, and contents must be restricted by vertical and horizontal barriers. Many measures accepted as necessary in building construction have not been applied in the construction of ships, mainly on account of added weight and cost. Recent developments in light-weight incombustible or fire-retardant materials have overcome these objections to a considerable extent.

The construction of fire-resistive bulkheads transversely across the ship has received recognition in recent years as essential in restricting horizontal spread of fire. According to the regulations adopted by the International Convention for the Safety of Life at Sea, these are required to be spaced at intervals not exceeding 40 meters (131 feet) and to be effective as a barrier for one hour against fires producing temperatures of 815° C. (1,500° F.) at the bulkhead. Uninsulated steel bulkheads have been advocated for acceptance under this

* Communicated by the Director.

requirement although obviously not meeting it because of ready transmission of heat through the metal. The results of fire tests as well as construction requirements have indicated, however, the desirability of incorporating the steel bulkhead as a part of the construction, with incombustible heat insulating materials applied on both sides. For the one-hour requirement, the total thickness of such materials need not exceed 2 inches and the weight need not be greater than 10 pounds per square foot. In building construction, fire barriers of comparable importance would be required to restrict the spread of severe fires for 4 hours. With proper choice of materials this can be effected with a thickness of 4 to 5 inches and weight of 20 to 30 lb./ft.^{2} As applied in ship construction the hull, decks, longitudinal bulkheads, and intersecting pipe lines would need insulation for a foot or two on each side of such bulkhead to prevent transmission of fire from heat conduction through the metal. Constructing intermediate longitudinal and transverse fire-resistive bulkheads and cabin partitions is considered desirable as an aid in further restricting the spread of fire. On account of limitations in thickness and weight, the fire resistance that can be practically attained for them would be in the range one-half to one-fourth hour as gauged by the standard fire testing procedure for fire partitions. Even so, as built of incombustible or fire retardant materials they would serve acceptably in confining the fire until detected and extinguished with the equipment provided.

Openings in the main fire resistive bulkheads need protection with automatically-closing or self-closing fire doors. Stairways, particularly those communicating between more than two decks, need fire resistive inclosures with lighter self-closing fire doors in the openings. The number and location of these stairways should be such as to afford egress to relatively safe areas in case of fire. Fire stopping the spaces between the deck and bulkhead plates and their linings at suitable intervals will prevent rapid spread of fire through such concealed channels.

Because of weight limitations, deck construction cannot be given as high a degree of fire resistance as floors in fire resistive buildings. Nevertheless, to judge from results of fire tests

with unprotected and protected welded steel floors, protection comparable with that given by one-hour bulkheads is obtainable with incombustible or fire retardent linings over the beam flanges. These should be one-half to one inch thick combined with an incombustible top finish over the deck plate of comparable thickness. These linings and finishes would replace the combustible boards and floor covering otherwise used in spaces occupied by passengers and crew. Mastics with low combustible contents and excellent strength, bonding, and wearing properties are now obtainable at moderate cost. They can serve as the finished wearing surface or as a base for the same.

Fire retardent treatments.—The general methods for treating wood to reduce its flammability involve imprengation with chemicals under pressure. No treatment has been developed that has the desired permanence as exposed to the weather, without protective coatings, but for interior use a number of them have been in practical use for the past 30 years or more. Specifications, inspection, and tests can be applied that will give fair assurance of obtaining a required fire retardent effect. A number of other requirements must be met by the material, including freedom from unduly corrosive effects on metal, unduly poisonous chemicals, hygroscopic chemicals, and surface discoloration. A full treatment increases the weight of the wood about 15 per cent. and the cost of hardwood finishing lumber about 100 per cent. Where combustible materials are prohibited by building ordinances, the product has found considerable application for finish flooring and interior trim, although in recent years displaced to some extent by metal trim and composition floor finishes.

Surface treatments of wood have only minor value in decreasing the flammability, on account of the thinness of the protecting coating. Ordinary oil paints with a relatively high mineral pigment content have been found as effective as so-called fire-retardent paints.

Draperies and curtains can be satisfactorily flame-proofed by spraying or dipping, using a number of chemical mixtures. A borax-boric acid treatment developed for treating theatre scenery has been found very effective, and the cost of the chemicals is relatively small. Such treatments must not de-

teriorate the fabric nor cause change in color or luster. The ordinary treatments are not permanent under laundering, although a treatment has been developed for cotton goods that gives fair resistance from this standpoint.

Satisfactory heat insulating and sound absorbing media can now be obtained of incombustible materials, and some of the combustible materials can be treated with admixtures, surface coatings, or veneers to reduce the flammability.

Cargo and Stores.—The properties considered hazardous include low flash, fire, and boiling points for liquids, low ignition temperature, high flammability, and susceptibility to spontaneous heating, liberation of oxygen, and detonation. Tests for such properties have been made of a wide range of materials submitted for ship cargoes and stores, necessitating in some cases extended experimental inquiry, among which may be mentioned the work on the effect of heat on celluloid (Bureau of Standards Technologic Paper no. 98, now out of print, but available at many technical libraries) as well as the heating and ignition tests with jute (Monograph, National Fire Protection Association, 1934).

Fire Detection.—According to an Act of Congress, all vessels more than 150 feet in length contracted for after June 30, 1916, which are provided with staterooms or other sleeping quarters for passengers, are required to be equipped with automatic fire-detecting systems for all spaces not readily open for inspection. In case of fire these detecting devices must give audible and visible alarm signals at the bridge and other points where a continuous watch is maintained. This constituted a considerable advance in safety requirements over those of many other maratime nations. Under this requirement tests have been made of the thermostats and other thermosensitive elements employed. The general designs of various systems have also been studied. As a result of these tests decided improvements have been made in sensitivity and reliability of operation of these devices, so that it is now possible to receive positive warning of a fire at an earlier stage than formerly, and there is less likelihood of failure.

Motion Picture Projection.—The showing of nitrocellulose motion picture film was formerly prohibited on ships of United States registry. The small range in subjects obtainable with

the slow-burning film and the difficulty experienced by inspectors in distinguishing between the two types, led to the adoption of safety measures that enabled the flammable film to be shown. Recommendations were drawn up for properly designed and vented projection booths, and examinations made of motion picture projectors for needed safety features. While it is more difficult to obtain a desired degree of safety on shipboard than in theatres on account of the use of portable booths and screens, the records show no instance of fire or jeopardy to life, resulting from the showing of motion pictures during the 12 years that these regulations have been in effect.

THE FABRICATION OF SILVER CHEMICAL EQUIPMENT.

As a part of a survey of existing and potential uses of silver made under a research associateship established at the National Bureau of Standards by a group of American silver producers, the field of silver chemical manufacturing equipment has been studied. An item on p. 92 of Technical News Bulletin No. 210 (October, 1934) covered the resistance of silver to corrosion by various agents. The methods of fabricating silver equipment are now being studied, as well as the properties of silver which are of special interest in this connection.

Silver has the highest electrical and thermal conductivities of any of the metals. Its softness and ductility are well known. Equipment which requires the use of silver may either be made entirely of fine silver or it may be lined by one of three methods: by fitting in thin silver linings, by electroplating, or by using a duplex material.

Fine silver equipment is the simplest to construct and is much used. It offers the advantage of easy reclamation of the silver when the equipment has served its useful life, since it does not have to be separated from another metal. The comparatively low strength of silver is a serious disadvantage for work at high pressure, particularly if the temperature is also high.

A common method of lining a piece of apparatus with silver is simply to fit silver sheets or other fabricated forms of silver snugly inside a shell of a base metal. The space between the lining and outer shell is made as small as possible by hammer-

ing the silver lining tightly against the casing. Such equipment is very serviceable and the silver can be easily reclaimed. The heat transmission of such apparatus is relatively poor.

Electroplated vessels of large size have been made but considerable care is necessary in doing the plating work if an impervious coating is to be obtained.

Duplex material consisting of silver joined to a base metal, for example a bimetallic sheet, has been used for small pieces, and interest is developing in the possibility of using this method in larger construction.

Silver can readily be soldered with either soft or silver solder. It can also be welded. When the sheets of silver are thick, the welding process may be carried out in much the same manner as in welding steel. Some operators use a flux while others prefer to weld the bare metal.

DETERMINATION OF COMBINED OXYGEN IN STEEL.

The importance attached by steel metallurgists to the project under way at the Bureau concerning the reliability of methods used for the determination of combined oxygen in steel is attested by the recent approval by the Iron and Steel Institute of Great Britain. Five research laboratories in that country have recently been encouraged by that Institute to participate in this coöperative study. This brings the number of coöperating foreign laboratories to 17, the total number engaged in the work being 37.

STRUCTURE OF WELDED STAINLESS STEEL.

Welding of stainless steel of the "18–8" type (18 per cent. chromium and 8 per cent. nickel) often results in a structural change, usually considered to be detrimental, wherein carbides are formed within and around the constituent grains. The use of certain metallographic etching methods for revealing this condition is frequently included in specifications, electrolytic etching in a solution of sodium cyanide being a common method. This method, although superior to most others, has a number of drawbacks. A new method recently used by the Bureau in a study of the changes induced in special alloy

steels upon welding, promises to be far superior to all others. This consists in etching electrolytically in oxalic acid (10 g. in 100 ml. of water), the specimen being the anode and a piece of platinum the cathode. The current from 3 standard dry cells in series or from a 6-volt storage battery serves to reveal carbides in the metallographic structure in 15 to 30 seconds and the grain structure on etching about 30 seconds longer. The solution does not stain the specimen—a drawback of almost all other methods.

GRAIN STRUCTURE OF STEEL WIRE.

Application of the McQuaid-Ehn carburizing test to specimens of heat-treated steel wire that failed in suspension bridge cables under low load showed that the steel did not respond uniformly. Both "normal" and "abnormal" steel were present in the wire. Although no one piece of wire was found that was entirely normal or abnormal as judged by the austenite grain size of completely carburized specimens, small sections were predominantly of one type or the other. The results of the McQuaid-Ehn tests indicate that wire showing low ductility when fractured under tension is predominantly "normal," that is, the grains of austenite (the high-temperature form of steel) are large, whereas wire with normal ductility had fine-grained austenite, or is "abnormal."

INSPECTION OF TIP OF WASHINGTON MONUMENT.

Advantage was taken recently of the scaffolding and other arrangements which have been made for the cleaning of the Washington Monument to inspect the aluminum pyramid which forms the tip of the Monument, 555 feet above the ground. This inspection was made at the request of Hon. Sol Bloom, Director of the George Washington Bicentennial Commission, by metallurgists from the Bureau and from the Aluminum Company of America. Aside from slight damage to the extreme tip of the aluminum cap by lightning, the aluminum was found to be in a remarkably well-preserved state. The surface of the cap was darkened by a thin gray oxide coating which could be easily scraped off so as to expose

the smooth silvery-bright metal surface beneath. The engraved inscriptions recording the placing of the cap 50 years ago (December 6, 1884) appeared as sharp and clear cut, after the oxide coating was removed, as if they had been finished only a relatively short time ago.

ANALYSIS OF FELDSPAR.

Feldspar, a mineral composed essentially of silica, alumina, and the oxides of sodium and potassium, and in addition varying small amounts of minor constituents, is of importance for the part it plays in the manufacture of numerous articles of commerce. Glass in its many forms, porcelain ware for both electrical and chemical purposes, chinaware and ornaments, and enamels for many different purposes are but a few of the manufactured products in which different grades of feldspar find use as an ingredient.

The methods commonly used for the chemical analysis of feldspar require an excessive amount of time, particularly if the analysis is to be used only for grading the material and great accuracy is not essential. More rapid methods have recently been developed at the Bureau, for the determination of alumina, calcium oxide, and the alkalies. In these, alumina is determined by precipitating with 8-hydroxyquinoline in acid solution and then titrating an acid solution of the precipitate. Calcium oxide is determined by precipitating with oxalic acid without prior removal of aluminum, and then titrating with standardized potassium permanganate. The alkalies are weighed as chlorides and potassium oxide is determined by separation and weighing in the form of its triple acetate. Optional methods may be used for decomposing feldspar by acid instead of by fusion.

COMPRESSIVE STRENGTH, YOUNG'S MODULUS OF ELASTICITY AND POISSON'S RATIO OF KEENE'S CEMENT.

Keene's cement is anhydrous calcined gypsum obtained by heating gypsum to about 1,000° C. The time of set of this dehydrated product is then accelerated by the addition of other materials.

In the course of an investigation of concrete, information was desired on the elastic properties of Keene's cement. Since no reliable data could be found, measurements were made of the lateral and longitudinal deformations under a compressive load on four prisms of the material. The wet mix contained 39 per cent. water by weight of Keene's cement. The prisms were 4 by 4 by 8 inches and they were cured for about 21 days at 37.7° C. Measurements of the deformations under load were made with Tuckerman's optical strain gages having a gage length of 2 inches.

The average values of the secant modulus of elasticity, Poisson's ratio, and the compressive strength were:

Compressive Stress, lbs./in.²	Modulus of Elasticity, lbs./in.² × 1,000,000.	Poisson's Ratio.
500	2.03	0.25
1,000	1.99	0.25
1,500	1.95	0.26
2,000	1.89	0.26
2,500	1.84	0.27
3,125	1.68	0.29

Compressive strength, 4,420 lb./in.²

Elimination of Rail Joints.—(*Science Service.*) It is estimated that the railroad industry would save $180,000,000 per year in decreased depreciation of equipment if only the little gaps between each rail were eliminated. If the rails were welded together, thus eliminating the quarter and half-inch spaces between the ends, the passengers would have a much quieter and smoother ride. To the railroads would come a saving because the life of the rails would be increased five years due to the absence of battering at the joints.

A question is then raised as to how expansion and contraction of the rail shall be taken care of. In the first place, engineers have observed that the actual change in rail length is always considerably less than theoretical. The plan is to weld the rail during the hottest months of the year when the rails reach their greatest length. When cooler weather comes and the rails try to contract the stress on a given cross-section may rise as high as 247,000 pounds to the square inch. While this may seem enormous it is well within the elastic limits of the steel and of the weld. Laid in such a manner there need be no fear that the rails will ever buckle up due to expansion.

C.

NOTES FROM THE BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

THE RELATION OF THE PRIMARY COSMIC RADIATION TO THE PHENOMENA OBSERVED.*

BY

W. F. G. SWANN, Director.

In a recent paper [1] the writer, discussing the significance of J. Clay's [2] observations of the cosmic radiation down to depths of 270 meters below water, amplified a view suggested in former communications to the effect that the primary cosmic radiation of corpuscular kind produces no ions until by the production of showers (singles, doubles, and many-ray groups) it has fallen in energy below a certain critical value. On this view the primary corpuscular radiation is to be regarded as passing through our atmosphere with a density (measured by *numbers* of rays per square centimeter, per second) which is independent of altitude. The apparent increase of intensity with altitude becomes really an increase in the number of secondaries (showers) resulting from increase of the energy (not number) of the individual primary rays with altitude. The purpose of this note is to amplify further this view. To avoid complexity we shall retain only the fundamental elements and shall confine ourselves to the approximation that the range of the secondaries is small compared with the effective thickness of the atmosphere, so that the ionization at any altitude is determined by the number of secondaries produced per centimeter per second at that altitude. We shall consider that the showers are all of the same kind.

We shall first consider the simplest case, where the number of showers N_s produced per c.c. by the primaries falling

* An article appearing in the *Physical Review*, November 1, 1934.

[1] W. F. G. Swann, *Phys. Rev.*, **46**, 432 (1934).

[2] J. Clay, *Physica*, **1**, 363 (1934).

in unit solid angle, at the angle θ to the vertical is

$$N_s = \alpha E, \tag{1}$$

where E is the energy of the rays and α is a constant. Since the rays lose energy by producing the showers, if x is an element of length measured along the path of the primary

$$\frac{dE}{dx} = -\beta N_s = -\beta\alpha E \tag{2}$$

when β is a constant. Thus

$$E = Be^{-\beta\alpha x} \tag{3}$$

and, from (1)

$$N_s = \alpha Be^{-\beta\alpha x},$$

so that the *observed* intensity in the direction determined by θ follows an exponential law with a coefficient of absorption $\beta\alpha$ although the primaries are *constant* with altitude as regards number per square centimeter per second.

We shall now take the next simplest case, where (1) is replaced by the more general form

$$N_s = \alpha_1 E + \alpha_2 E^2 + \cdots \text{etc.}, \tag{4}$$

in which α_2, α_3, etc. are such that the corresponding terms are small compared with the term $\alpha_1 E$. Equation (2) then becomes replaced by

$$\frac{dE}{dx} = -\beta N_s = -\beta\alpha_1 E - \beta\alpha_2 E^2 + \cdots \text{etc.} \tag{5}$$

Solving this approximately by neglecting all terms involving higher powers of E than the first, we obtain, as in (3),

$$E = B_1 e^{-\beta\alpha x},$$

Substituting this in the terms of (5) involving E^2 and higher powers, we have

$$dE/dx + \mu E = -\beta B_1^2 \alpha_2 e^{-2\mu x} - \beta B_1^3 \alpha_3 e^{-3\mu x} + \cdots \text{etc.},$$

where $\mu \equiv \beta\alpha_1$. The solution of this takes the form

$$E = Be^{-\mu x} + (\beta B^2\alpha_2/\mu)e^{-2\mu x} + (\beta B^3\alpha_3/2\mu)e^{-3\mu x} + \cdots \text{etc.} \tag{6}$$

and N_s, and so the measured intensity for the direction concerned, takes the form

$$N_s = \alpha_1 B e^{-\mu z} + 2\alpha_2 B^2 e^{-2\mu z} + \cdots \text{etc.}$$

The significant thing is that, starting with a primary radiation whose intensity (as measured by numbers of rays) is independent of altitude, we have arrived at an expression for the measured intensity which involves a contribution from a series of terms with absorption coefficients μ, 2μ, 3μ, etc. However, our hypothesis as to the smallness of α_2, α_3, etc., would presumably render these "harmonics" unobservable, and the fundamental would correspond to that coefficient $\mu = 0.5$ per meter of water, cited by Millikan as representative of 90 per cent. of the radiation observed.

Bearing upon Variation of Stoss Production in Lead with Altitude.—As part of a general program of investigation of stoss production, in this laboratory, Dr. and Mrs. Montgomery have measured the rate of production of stösse in lead at the summit of Pike's Peak, at Colorado Springs, and at sea level. The results, as yet unpublished, give a large increase with altitude, an increase much larger even than would correspond to the absorption coefficient of the softest component of the measured cosmic radiation. Now by considering matters in the light of the theory given above, I think it is possible to see, in a natural way, how this may come about. Suppose that in the fundamental equation (4) which tells the story of stoss production as a function of energy, the coefficients α_1, α_2, α_3, are functions of the atomic number A of the material in which the stösse are produced. Suppose, for example, α_2 were proportional to A^n, and the other coefficients were independent of the A. Then it might well be that while the $\alpha_2 E^2$ term was negligible for air it might be all important for lead. The story of the variation of E with altitude would go on as before and would involve only the constants characteristic of air. When, however, we came to calculate the rate of production of the stösse in lead, it would be the α_2 term which was now significant, so that the stoss production at two altitudes would be determined by the ratio of the values of E^2 at those altitudes,[3] and so, by the ratios of the

[3] To be meticulously exact we should say "for any given direction."

squares of the right hand sides of (6) for the two cases. The preponderant term involving $e^{-\mu x}$ in (6) will give rise to a term $e^{-2\mu x}$ so that the rate of stoss production with altitude in lead will be twice that in air. If the α_3 term in (4) increased rapidly with the atomic number, the stoss production in lead would show a rate of increase with altitude three times that for the main component of the apparent cosmic radiation. In general we may expect all of the α's to be functions of the atomic number so that the actual story may be expected to be more complicated in algebraic form, but not in quantitative significance.

CONCERNING THE FLUCTUATIONS OF CURRENT IN A HIGH RESISTANCE.

BY

GEORGE W. BARNES.

In the construction of an amplifier for the measurement of cosmic ray ionization, it was found that the introduction of metallized resistors into the plate circuits caused a short period fluctuation in the amplifier. This effect was also observed by A. W. Hull [1] in connection with his work on the Schottky effect in vacuum tubes. He found that when the tube was replaced by a wire-wound resistor, there was no observable fluctuation, but that an india ink resistor gave rise to fluctuations of the same size as the Schottky effect. However, he did not comment on the observation.

The resistors in question consist of metallic films on glass. It was suggested by Dr. W. F. G. Swann that if conduction in these films takes place by leaps of electricity between aggregates or groups of molecules in the film, the phenomena ought to partake of the nature of a Schottky effect, but with the electronic charge replaced by an apparent electronic charge of much larger magnitude, and characterized by the sizes of the spurts of electricity functioning in the sporadic leaps above referred to. The object of the present experiments was to verify this matter.

This paper covers a preliminary study of the variation of the fluctuation, with the total current through the resistor.

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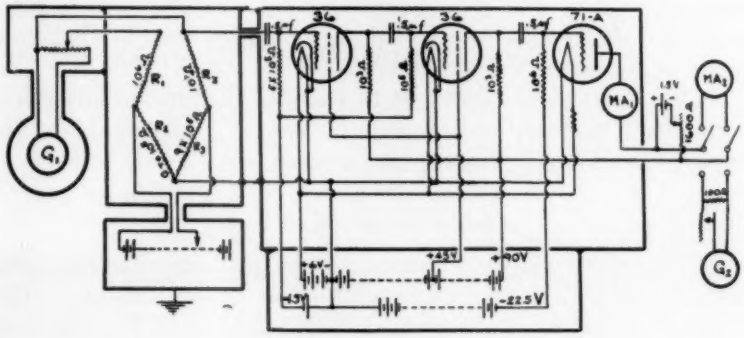
[1] A. W. Hull and N. H. Williams, Shot Effect, *Phys. Rev.*, **25**, 1925, p. 173.

A commercial 10 megohm "metallized" resistor was used. As a check this was replaced by a water resistor, and later by a wire-wound resistor. Neither of these caused any fluctuation comparable to that caused by the metallized resistor.

FIG. 1.



DESCRIPTION OF APPARATUS.

A schematic diagram of the apparatus is shown in Fig. 1. The resistance to be studied was arranged in a Wheatstone bridge circuit so as to eliminate possible battery fluctuations. Resistances R_1, R_2, and R_3, were all wire-wound. The source of potential was a bank of "B" batteries. Galvanometer G_1 at a sensitivity of 5×10^{-7} A/mm. was placed in series with the metallized Resistor R_x. This galvanometer, at a higher sensitivity and with one connection changed, was also used to balance the Wheatstone bridge. It is interesting to note that in balancing the bridge, it was observed that the resistance of the "metallized" resistor varied from 14.8 to 10.5 megohms, as the current flowing through it was increased.

The amplifier, composed of three capacity-coupled stages, was, with the exception of a very few changes, a copy of that used by Dr. Swann in his experiment with small ionization chambers. It was calibrated directly by impressing .001 volt on the grid of the first stage. The amplifier, batteries, and bridge, all had to be carefully shielded to prevent pick-up of foreign electrostatic disturbances, particularly 60 cycle.

The fluctuations were indicated by a short period galvanometer G_2. Its characteristics were:

Sensitivity	2.4×10^{-6} Amp./mm.
Resistance	4.8 Ohms
Critical Damping Resistance	2 Ohms
Period	1/40 second

It was connected directly in the plate circuit of the 71-A tube, the steady plate current being balanced out by an opposed current. MA_1 was a milliameter used to indicate the plate current. MA_2 was used to roughly balance the circuit before the galvanometer was connected.

The deflections were recorded on Eastman Recording paper in a hand-driven recording camera. The speed of the paper was about 1.5 inches per second.

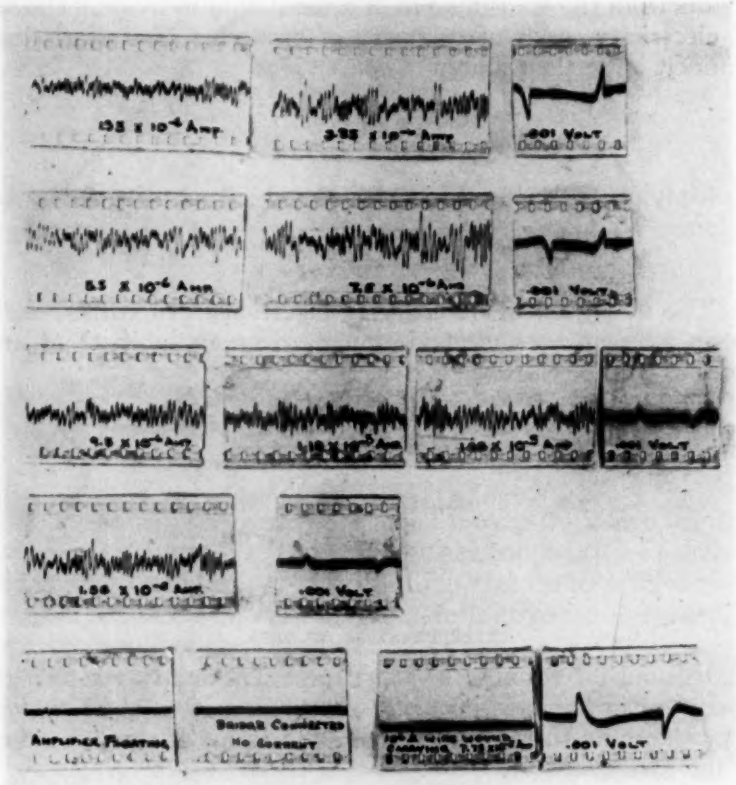
METHOD OF OBTAINING DATA.

The potentials were connected to the amplifier an hour before it was used, so that it might come to equilibrium before data were taken. A trace was then taken with nothing connected to the input. With the amplifier and batteries carefully shielded, there was only a small fluctuation. Most of this was probably due to mechanical vibration and shot effect in the first tube. The bridge was then connected, with no current flowing through it, and a trace taken. The fluctuation was still negligible. Then a series of potentials was applied across the bridge. In each case the bridge was balanced, the current through the "metallized" resistor was measured, and a trace of the fluctuations over a period of twenty seconds was taken. When necessary, the sensitivity of the apparatus was reduced by adding resistance in series with the galvanometer. The characteristics of the amplifier were kept constant. Samples of the traces are shown in Fig. 2.

The size of deflections was measured on each side of a line through the approximate center of the trace. Measuring on both sides eliminated any possible error from mis-judgment of the center. Roughly, five hundred "kicks" were measured for each current.

The trace at the extreme right of each line indicates the sensitivity of the apparatus. It is the "kick" produced by impressing .001 volt on the grid of the amplifier.

FIG. 2.



SAMPLES OF TRACE.

THEORETICAL CONSIDERATIONS.

For the purpose of this discussion, a theorem from the theory of probability is required: If δn is the deviation of a number of events in an interval Δt from the average number $\bar{n}$ in intervals of length Δt, and if N is the total number of observations of length Δt, then the mean of the deviations squared is equal to the average number of events $\bar{n}$.

$$\text{(I)} \quad \overline{\delta n^2} = \bar{n}.$$

The δn in formula (I) is a deviation in number of events per time interval Δt, and $\bar{n}$ is the average number of events in

this interval. We shall assume that the average current I_x results from the transmission of a number of individual spurts of electricity, each of quantity q, occurring in a statistical manner. We then write,

$$I_x = \frac{\bar{n}q}{\Delta t}, \qquad \text{whence} \qquad \bar{n} = \frac{I_x \Delta t}{q},$$

multiplying both sides of (I) by q^2 and substituting for $\bar{n}$ we obtain

$$\overline{(q\delta n)^2} = qI_x\Delta t.$$

The deviation in quantity of electricity $q\delta n$ corresponds to an average current deviation Δi over an interval Δt according to the relation

$$q\delta n = \Delta i \Delta t$$

and the equation becomes

$$\overline{(\Delta i \Delta t)^2} = qI_x\Delta t,$$

$$\overline{(\Delta i)^2} = \frac{qI_x}{\Delta t}.$$

INTERPRETATION OF DATA.

It is our intention to find an expression for ΔI_x, the change of current in R_x, in terms of the change of potential ΔV which it produces on the amplifier, and so in terms of the deflection of the galvanometer.

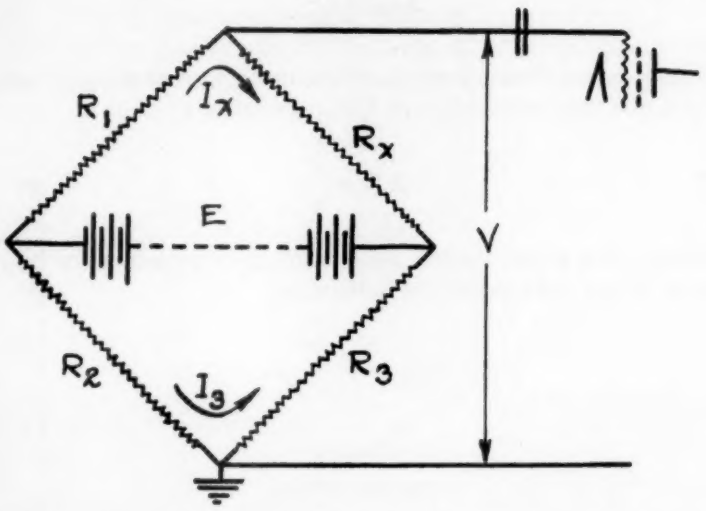
In Fig. 3 is shown the bridge arrangement. R_x is the resistor being studied. R_1, R_2, R_3 are wire-wound resistors with fluctuations in conductivity negligible compared to those in R_x. E is the potential of the battery, and V the potential difference across the bridge, which is equal to the difference of the voltage R_xI_x across R_x and the voltage R_3I_3 across R_3.

When the bridge is in a balanced condition

$$V = R_xI_x - R_3I_3 = 0.$$

When, however, the resistance of R_x changes by ΔR_x, I_x changes by ΔI_x, and the potential drop across R_x changes by ΔV_x. Now, since V_3 remains constant, there will be a potential difference across the bridge of ΔV which will be equal to

FIG. 3.



ΔV_x, provided the resistance in the output branch of the bridge is infinite. Since the bridge was coupled to the amplifier through a capacity, this condition was sufficiently closely realized to justify the assumption of infinite resistance—which greatly simplifies the calculations.

We could express ΔV in terms of R_x, ΔR_x, I_x, and ΔI_x. This is a rather complicated function. However

$$V_x + V_1 = E$$

and since E remains constant then there must be a change in the potential drop across R_1 of ΔV_1 equal and opposite to ΔV_x.

$$\Delta V_1 = -\Delta V_x = \Delta V.$$

As R_1 is constant ΔV_1 may be expressed in terms of R_1 and ΔI_x, thus

$$\Delta V_1 = R_1 \Delta I_x.$$

Now since sign is not important we may write

$$\Delta V = R_1 \Delta I_x.$$

Solving for ΔI_x we get an expression for the change in current through R_x in terms of the voltage across the bridge.

$$\Delta I_x = \frac{\Delta V}{R_1}.$$

ΔV may be expressed in terms of the deflection of the galvanometer d and the sensitivity of the apparatus s.

$$\Delta V = \frac{d}{s}.$$

Substituting these values we obtain an expression for ΔI_x in terms of the galvanometer deflection.

$$\Delta I_x = \frac{d}{s \times R_1}.$$

TABLE 1.

Summary of Data.

Current Through R_x ($\times 10^6$).	$\sqrt{\text{Current}}$ ($\times 10^3$).	R.M.S. Deflection.	Sensitivity of Amplifier mm./10^{-6} Volt.	R.M.S. ΔV Volts $\times 10^3$.	R.S.M. Δi Amps. 10^{10}.
1.35	1.16	1.53	7	2.2	2.4
3.35	1.83	2.95	7	4.2	4.7
5.5	2.35	2.41	4	6.0	6.7
7.5	2.74	3.64	4	9.11	10.1
9.5	3.08	2.09	2	10.5	11.6
11.8	3.44	2.35	2	11.8	13.1
13.8	3.72	2.77	2	13.9	15.5
15.8	3.97	2.47	1.6	15.4	17.1

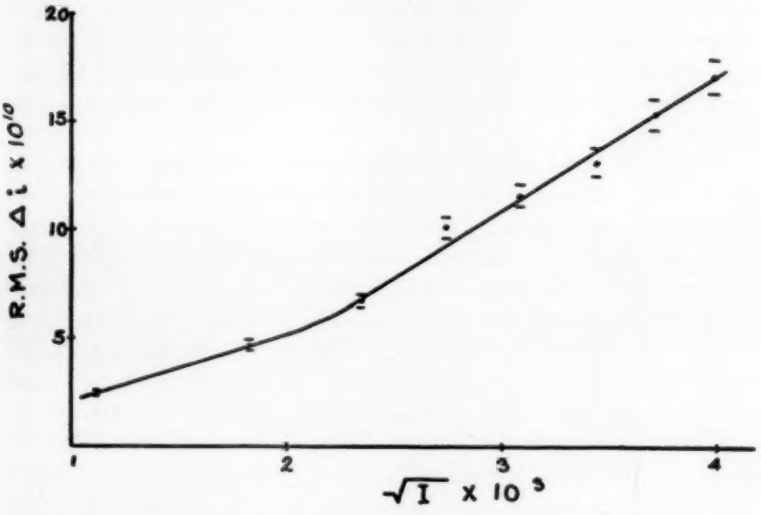
The ΔI_x in this relation represents instantaneous change of current. The theory however requires the quantities represented by Δi which are current deviations averaged over equal intervals Δt. We shall assume at this point that these intervals are provided by the period of the galvanometer, and that each peak deflection d_0 is proportional to a Δi corresponding to an interval Δt. For purpose of a rough calculation of q it will be further assumed that the relation between Δi and d_0 is the same as that between ΔI_x and d. We then write

$$\overline{(\Delta i)^2} = \frac{\overline{d_0^2}}{S + R}.$$

This computation was carried out for the experimental data. The figures are given in Table 1.

Our theory has suggested that the R.M.S. Δi should vary as the square root of I_z. In Fig. 4 the quantities are plotted

FIG. 4.



in this form and it is seen that this prediction of the theory is approximately fulfilled. This agreement is independent of the assumption regarding the constant of proportionality between Δi and d_0.

The actual calculation of q, however, does involve this admittedly inaccurate calibration, and hence will only have meaning as regards order of magnitude. Carrying it out, however, we find $q = 3.4 \times 10^{-8}$ e.s.u., which is about 72 times the charge on one electron.

The author wishes to express his thanks to Dr. W. F. G. Swann, who suggested the investigation, and under whose direction it was carried out, and also to Dr. William E. Danforth, for criticism of the paper.

CONCERNING THE RECOVERY TIME OF GEIGER-MUELLER COUNTERS.*

BY

W. E. DANFORTH.

We have equipped a Braun Tube with a timing "sweep" which is initiated by the phenomenon to be studied. Thus, pulses recurring at random will give retracing curves on the fluorescent screen and so may be photographed. Figures (1–3) show three oscillograms with a schematic diagram at the right of each.

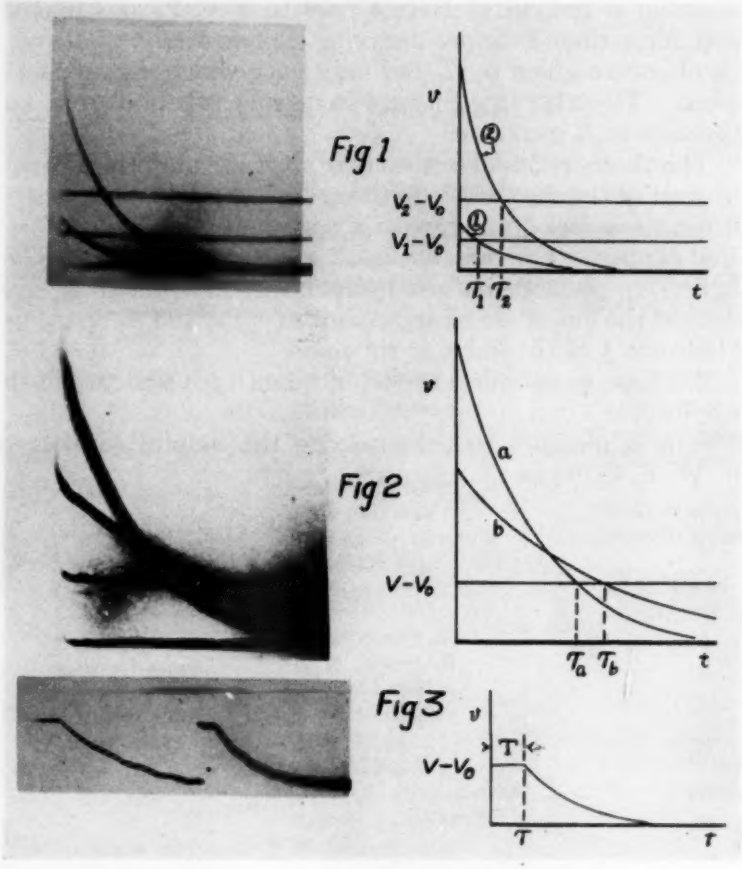
The ordinates of the curves represent the negative potential v of the wire of a Geiger-Mueller counter connected in the usual way, namely, with the outer cylinder at constant (negative) potential V, and the wire grounded through a high resistance R. Figures 1 and 2 show that when a discharge occurs, v rises suddenly and then falls following an exponential curve. As one would expect its time constant is equal to RC where C is the total capacity between the wire and ground. Curves 1 and 2 in Fig. 1 show discharges for two values V_1 and V_2 of the applied voltage. The horizontal lines $V_1 - V_0$ and $V_2 - V_0$ show the excess of V over the starting potential V_0. In other words $V - V_0$ represents that value of V for which the voltage across the counter equals the starting voltage.

By suddenly applying x-radiation we have seen that a counter will discharge after v has fallen below $V - V_0$ but not before. Therefore, the recovery times for the respective systems are defined by the associated time intervals denoted by the τ's in the oscillograms.

In Fig. 1 V_2 is greater than V_1, so one sees that the excess of the initial value of v over $V - V_0$ increases with increasing V. Therefore the time τ is larger for higher operating voltages.

The two curves in Fig. 2 were taken with the same applied voltage V. In curve b the value of C was about twice that in curve a. This increase of C has increased the time constant of the curve but decreased the initial ordinate. The former

* An article appearing in the *Physical Review*, Dec. 1, 1934.



change tends to increase τ while the latter tends to diminish it. In this particular case, doubling C has increased τ by about 27 per cent. It seems quite possible that in some cases increasing C may actually decrease τ.

If a pulse occurs before the v of a preceding one has fallen to zero, it will be smaller than the preceding pulse and have a smaller τ. So for very rapid counting rates one has a statistical distribution of τ's.

For higher values of V or C, the discharges may take the form shown in Fig. 3. This is a photograph of a single sweep during which two discharges occurred. (Some 60 cycle

induction is present.) Here v rises to $V - V_0$ and remains there for a time T before decaying exponentially. The time τ is of course given by T and may vary widely in successive pulses. The average T is an increasing function of C and decreases as R increases.

The observations described here are quite uniform throughout a set of counters made in the same "batch." The wire in all counters was 3 mil tungsten and the cylinders were oxidized copper. The pressure in all cases was 7 or 8 cm. The qualitative phenomena are independent of counter size, of whether the gas is air or argon and oxygen, and of change in R between 5×10^8 and 5×10^9 ohms.

We hope to submit a report of quantitative nature in the near future.

It is a pleasure to acknowledge the helpful support of Dr. W. F. G. Swann.

THE FRANKLIN INSTITUTE.

STATED MONTHLY MEETING, DECEMBER 19, 1934.

The regular monthly meeting of the Institute was called to order by the President, Mr. Nathan Hayward, at eight-fifteen P.M.

The Secretary reported that this was the night for the nominations for officers and members for the new terms beginning with January 1935. He then presented the following nominations:

Office	*Nominee*	*Nominated by:*
President	Nathan Hayward	R. W. Lesley Benjamin Franklin M. S. Morgan
Vice-Presidents	Walton Forstall	
	Henry Howson	S. M. Vauclain
	W. Chattin Wetherill	James S. Rogers
	Samuel S. Fels	
Treasurer	Benjamin Franklin	James Barnes Lewis G. Schlehner
Board of Managers	Henry Butler Allen	
(To serve three years)	G. H. Benzon, Jr.	
	G. H. Clamer	
	A. W. Goodspeed	
	L. H. Kinnard	C. D. Galloway
	Charles Penrose	Nicol H. Smith
	George D. Rosengarten	Alfred Rigling
	Samuel M. Vauclain	
(To serve one year)	R. W. Lloyd	
(To serve one year)	O. J. Matthews	
(To serve two years)	C. C. Tutwiler	
(To serve two years)	W. H. Fulweiler	

He stated that members had the right to offer other nominations from the floor. The President called for such nominations but none being presented he declared that the nominations were closed. The list of nominees proposed by the Secretary will be incorporated upon the regular ballot which will be sent to the members of the Institute for the election to be held in January.

The Secretary made special reference to the Christmas Week Lectures which will be held on December twenty-sixth, twenty-seventh and twenty-eighth.

The Secretary then called to the attention of the President the fact that a ceremony had been arranged by which the Bausch and Lomb Optical Company would present to the Institute a plaque commemorating the One Hundred and Fiftieth Anniversary of Bifocals for Spectacles, invented by Benjamin Franklin

in 1784, and stated that the presentation would be made on behalf of the Bausch and Lomb Company by Dr. George S. Crampton. The President then called upon Dr. Crampton who presented the plaque very pleasingly and quoted portions of two original letters in which Franklin describes his invention of the Bifocal Lenses. The President accepted the medallion on behalf of the Institute and requested that Dr. Crampton convey to the Bausch and Lomb Company his expression of appreciation on behalf of The Franklin Institute.

There being no further business, the President then presented as the speaker of the evening Dr. George G. Brown of the University of Michigan who spoke on "Solution Cycles as Applied to Step-Up Transformers for Temperatures."

Dr. Brown delivered a masterly paper on this suggestive new field of physical science. At the close of his paper, he showed a practical application of this new subject to the important matter of air-conditioning and showed how it could be used to determine the cost of air-conditioning by different methods now in use. The lecture was followed by a number of questions from members of the audience, who seemed greatly interested.

The meeting was adjourned by President Hayward with an expression of appreciation for Dr. Brown's really masterful talk.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, December 12, 1934.)

HALL OF THE COMMITTEE,
PHILADELPHIA, DECEMBER 12, 1934.

MR. CHARLES D. GALLOWAY *in the Chair.*

The following reports were presented for final action:

No. 2954: High Power Microscopy.

This report recommended the award of the John Price Wetherill Medal to Dr. F. F. Lucas, of the Bell Telephone Laboratories, "In consideration of his development of a technique of microscopy and photomicrography by virtue of which objectives of the highest numerical aperture yet developed and visible light and ultra violet light have been brought to their full theoretical resolving power, and by the use of which photomicrographs of metallurgical and biological specimens superior to any heretofore made are now being produced under his direction."

No. 2987: Visagraph for the Blind.

This report recommended the award of the John Price Wetherill Medal to Mr. Robert E. Naumburg, of Cambridge, Massachusetts, "In recognition of his invention of the Visagraph for the Blind which embodies a meritorious utilization of several well-known mechanical and physical principles to produce an apparatus original in its accomplishments and of unquestioned benefit to humanity."

The following report was presented for first reading:

No. 2964: Stroboscope and Portable Dynamic Balancing Equipment.

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

RESIDENT.

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LIBRARY NOTES.

RECENT ADDITIONS.

American Institute of Chemical Engineers. Transactions, 1933–34, Volume 30, 1934.

BARNARD, ROY M. Radio Receiver Measurements. No date.

BERNHEIM, G., AND M. GUYOT. Traité d'Analyses par les Rayons Ultra-Violets Filtrés. 1932.

BROOME, DONALD C. The Testing of Bituminous Mixtures. A Laboratory Handbook Concerning Road and Building Materials. With a Chapter on Roofing Felts by R. O. Child. The Roadmakers' Library. Volume 2. 1934.

Chemical Engineering Catalog. Nineteenth Annual Edition. 1934.

FALKENHAGEN, HANS. Electrolytes. Translated by R. P. Bell. 1934.

FAVARY, ETHELBERT. Motor Vehicle Engineering. Engines: their Design and Construction (for Automobiles, Trucks and Tractors). Third edition. 1927.

FAVARY, ETHERLBERT. Motor Vehicle Engineering. The Chassis. First edition. 1922.

FISCHER, HANS, UND HANS ORTH. Die Chemie des Pyrrols. 1 Band: Pyrrol und seine Derivate, mehrkernige Pyrrolsysteme ohne Farbstoffcharakter. 1934.

GARNER, H. H. Collected Reports on British High Speed Aircraft for the 1931 Schneider Trophy Contest. Aeronautical Research Committee. Reports and Memoranda No. 1575. 1934.

GREGG, J. L. Arsenical and Argentiferous Copper. American Chemical Society. Monograph Series No. 67. 1934.

HOLLUTA, JOSEF. Die technischen Anwendungen der physikalischen Chemie. 1934.

JEANS, SIR JAMES. Through Space and Time. Based on the Royal Institution Lectures, Christmas, 1933. 1934.

KNOWLTON, ARCHER E. Electric Power Metering. A Textbook of Practical Fundamentals. First edition. 1934.

MALLETT, E. Vectors for Electrical Engineers. 1933.

MARTIN, THOMAS. Faraday. 1934.

NIERENSTEIN, M. The Natural Organic Tannins. History: Chemistry: Distribution. 1934.

Peddle, C. J. Defects in Glass. 1927.

Penrose's Annual, the Process Year Book. Volume XXXVI, 1934.

Philadelphia. Free Library. Exercises at the Opening of the Main Building of the Free Library of Philadelphia, Facing Logan Square, June 2, 1927, at Four O'Clock. 1927.

SCHULTZ, GUSTAV. Farbstofftabellen. Siebente Auflage neu bearbeitet und erweitert von Dr. Ludwig Lehmann. Ergänzungsband 1 umfassend die Literatur bis 31 Dezember 1933. 1934.

WILSON, W. Theoretical Physics. Volume 1: Mechanics and Heat, Newton-Carnot; Volume 2: Electromagnetism and Optics, Maxwell-Lorentz. 1931–1933.

BOOK REVIEWS.

ARSENICAL AND ARGENTIFEROUS COPPER. By J. L. Gregg, Metallurgist, Battelle Memorial Institute. 189 pages, with tables and 56 figures; 15.5 × 23.5 cms. American Chemical Society Monograph No. 67. The Chemical Catalog Company, Inc., New York, 1934. Price $4.00.

This briefer monograph of the Americal Chemical Society series is closely packed with facts and figures relating not only to arsenical and argentiferous copper but to electrolytic and other grades. It is a mine of information to those having to deal with copper or its alloys.

It has not been as generally realized as it will henceforth be due to this publication that certain of the properties of copper can be desirably modified by the presence of small and frequently natural proportions of silver and arsenic. In the author's words, "Users to whom electrical and thermal properties are paramount considerations will prefer non-arsenical copper, since arsenic to the extent of 0.1 per cent. lowers the electrical and thermal conductivity 25 per cent. But whenever improved rolling properties, strength, a higher annealing temperature or resistance to wear or to the principal corrosive agencies are desirable, the arsencial variety is generally to be preferred. . . . For purposes where ordinary copper falls short of certain requirements . . ., arsenical copper is often the wisest choice, as it is one of the most easily obtained copper-rich alloys and probably the least expensive of all." The major advantages of argentiferous copper lie in the ability of silver to raise the low annealing temperature while at the same time effecting but a low reduction in electrical and thermal conductivity. The necessity for the retention of strength at higher temperatures made possible by the addition of silver to copper or arsenical copper will be appreciated in connection with its use for firebox plates or in the assembly of automobile radiators by soldering or in electrical appliances which must be enameled and baked or soldered at temperatures above the annealing point of pure copper.

Chapter I is of general and historical interest. Chapter II covers the properties of pure copper. Other chapters cover geology and metallurgy, constitutional diagrams of the copper-silver, copper-arsenic and copper-oxygen systems, electrical and thermal properties, mechanical properties, and uses of arsenical and argentiferous copper. Another chapter deals with corrosion. A collected bibliography carries 161 entries.

Appendices give valuable information as to world distribution of copper production, price fluctuations of copper over a fifty-year period, comparative

prices of many metals and alloys for a number of years, standard wire tables, certain A.S.T.M. specifications, and the dimensions of various forms of cast standard ingots, billets, etc.

The volume appears almost free from serious errors. At the top of page 140 the formula for cupric oxychloride is incorrectly given.

LESLIE R. BACON.

TECHNICS AND CIVILIZATION, by Lewis Mumford, 495 pages, plates, 16 × 24 cms. New York, Harcourt, Brace and Company, 1934. Price $4.50.

Here is a book to make the mind work. The kind of book that cannot be read in a hurry. The sort of a book that requires close reading, that compels one to lay aside the current cares, and in the evening, sit with this book—sometimes reading and then thinking, to read some more and again drift into thoughtful reverie. Finally, after ten pages or so, one can stretch into a terminal yawn, declaring with a clear conscience that enough heavy work has been done in one day. It is good to work through a book like "Technics and Civilization."

Lewis Mumford has assailed the task of describing the machine as it has come into civilized life, the impact of the machine on men and the effect, in turn, that men have had on the machine. To sketch this course over the span of one thousand years is not easy. To describe the machine as the expression of the stuff that dreams are made of, as the output of the mind, as a projection of the interior world that lies encased within the skull, as a thing set apart from life and yet of the very fibre of life, is bold work. Mumford writes in bold strokes, dealing with art, life, customs and manners, each in a different way profoundly affected by the machine.

What are some of the sharper outlines that stand out at the end of the 435 pages? As a matter of fact one should be somewhat more objective in resumé and allow a week, a fortnight, possibly a month pass by and then evaluate the clear strokes. The following random ideas are distinctly reading residue.

After a long period of preparation, which intellectually took place for the most part within the walls of the monasteries of the Middle Ages a machine emerged as a fruit of order. The peace, security and regularization of religious life produced the clock and soon thereafter the watch evolved. It still hangs on my torso and ticks away the seconds of life as blithely as if it were invented yesterday. When it was first made, it brought into the world arrangement, reasonableness and order. Time became a moment. The day was divided. Hours laid their hands on the shoulder of life. Minutes began to count and seconds were to be reckoned. These insistent ticks of a machine have changed life from cock-crow to sunset, from hit or miss living to exact time. Sailings on the high seas are so many hours, minutes and seconds west of Greenwich. The drill of the alarm clock is heard on the frosty morning, and the split second of a flashed signal is traceable to the watch, *the* machine!

Another idea gained from this book still vivid and still fresh is the way the machine has divided life into the three stages, the eotechnic, the paleotechnic and latterly the neotechnic phase. Three meaty chapters cover these three phases, pages 106 to 269. All a review can do is to hint at main lines of thought. In a word the eotechnical phase is the period of wood, stone and glass as they appeared in the mechanics and the materials of living. Incidentally, it was during this period that Europe slew its forests to get the wood to make the houses, to build the

carts, to lay the rails, to carry the wooden wheels and so on down an endless road. Wind and water were prime movers. The windmills of Holland are picturesque survivors and the clipper ship under full sail is one of its finest symbols.

Iron entered, hand in hand, with coal and we have the period of paleotechnic. In a spirit of prophetic apostrophe, Dr. Erasmus Darwin wrote:

> Soon shall they arm, unconquered steam, afar
> Drag the slow barge, or drive the rapid car;
> Or on wide-waving wings expanded bear
> The flying chariot through the fields of air.
> Fair crews triumphant, leaning from above,
> Shall wave their flutt'ring kerchiefs as they move
> Or warrior bands alarm the gaping crowd,
> And armies shrink beneath the shadowy cloud.

Inserting the gas motor where Darwin in 1791 saw the steam piston, the sight is not so far fetched. Unfortunately Mumford does not allow the reader to tarry with much comfort on the coal-and-iron age. He underscores the incessantly evil conurbation of city populations from the cramping effects of which the airplane may help us fly. He stresses the destruction of environment wherever the factory has pocked the face of the land, the belching of gas sewage into the air and liquid offal into every stream, killing the fish, poisoning the air and producing a race of men (page 175) diseased, crippled, stupified and reduced to apathy and dejection by the paleotechnic environment only, up to a certain point, so much the better adapted to the new routine of factory and mill. "For," he says "the highest standards of factory efficiency were achieved with the aid of only partly used human organisms—in short, of defectives."

And a lot more along the same line in describing the House of Terror where industrialists and workers were inmates as jailer and prisoners, hating each other with that bitterness that finds but one conclusion, the blasting ennui of WAR. The profit system, the sexual prostitutions, the abysmal fatigue, the resort to opiates would all seem as unreal as a bad dream if one did not see the smoke of the mills fouling the air, the shredded sewage twisting and boiling in the Delaware river and the sick faces in the subway crush. Religion has been said to be the opiate of the people, but Mumford gives it a new twist and says that opiates became the religion of the people of the paleotechnic phase in which we still linger.

A ray of hope enters with the neotechnical phase. It is the new time, the period of "clean" electricity, reforestration, the restored environment, the light alloy and the activating force of the photo-cell. The beginnings of a new world when men are commencing to creep back to health, when sexual experience will be disassociated from marriage, when fine bodies will bathe in the sun, when fineness will be in demand with efficiency and beauty. Again it seems of the stuff dreams are made, if it were not for the photo-electronics on exhibit in the Franklin Museum, if it were not for the restoration of health hinted at in the new leisure, the ever more frequent nudism, the purified water course, the great electric power plants and a movement to purge life of its offal.

And, after you have looked at all the interesting pictures, cleverly packed and read the ten pages of listed inventions and the twenty-seven pages of bibliography, with running comment on most of the source matter, you will put the book down and ponder even until the dawn.

H. W. ELKINTON.

SCIENTIFIC ORGANIZATIONS IN SEVENTEENTH CENTURY FRANCE (1620–1680), by Harcourt Brown, M. A. Toronto, Ph.D., Columbia, 306 pages, 14.5 × 21.5 cms. Baltimore, The Williams & Wilkins Company, 1934. Price $3.00.

This book treats an interesting and critical period in the development of science in France. Great things were astir in the Seventeenth century. Anyone who has a particular drawing to this time bracket of scientific evolution and to the French scene will find an informing and a very well put together book.

There is an interesting detour against the perpetual motionists (page 35):

> "It would be a fine thing if one could disabuse all those who waste their time in the search for an artificial perpetual motion. . . ."

One might add, their time and other people's money. There is another rather diverting strip that refers to the introduction of telescopes into Paris where they were the "rage" by the middle of the Seventeenth century.

> "Vous devriez brûler tout ce meuble inutile,
> Et laisser la science aux docteurs de la ville;
> M'ôter, pour faire bien, du grénier de ceans
> Cette longue lunette à faire peur aux gens,"

Aside from the serious purpose of the book, there are many quotations of old French which have a certain aroma of old perfume. Dr. Brown or the publishers have submitted to the attractive French tradition of uncut pages. An ingenious compromise has been struck as the pages are uncut but intermittently slotted, so that a pen holder or leathery index finger can part the pages and so spare a sharp edge paper cutter. The book is excellently documented. It carries the stamp of a scholar.

H. W. ELKINTON.

CREATION'S DOOM, by Desiderius Papp, translated from the German original "Zukunft und Ende der Welt," by H. J. Stenning, 288 pages, illustrations, 15 × 21.5 cms. New York and London, D. Appleton-Century Co., Inc., 1934. Price $3.00.

Herr Papp attempts the forecast of the fate of our planet and our race—homo sapiens. In some ways his book is fantastic, in other ways too true. An excellent book to read if one is carried to the dizzy height of a sudden fortune. Or if stretched on a hospital cot one seeks solace in reading of persons in much greater distress.

The three divisions of the book deal with the Future, the Catastrophe and the End. A quick reader can vault to the end and read most of the new material with sporting ease. The bald-headed, toothless, earless ultimate man with an enlarged head can entertain along the way with possibly a peep into the incubator where the "ectogenetic sucklings" are getting their start. Finally the insects come into their own after the order of mammals has succumbed. There is a suggested contest between termites and ants with the ants gaining the battle because the waning sun will rob the termites of the necessary heat. In the meantime we keep the bugs down—with a constantly decreasing success.

This ant order reminds me of a grand show of ant husbandry which I had on dwarf apple trees in my garden a few summers ago. The ants had brought their herds of aphides to pasture on the leaves. They were doing a good milking busi-

ness when the tree expert engaged to spray for the Japanese beetle soaked the hedge of my dwarf apples. It did the leaves good but the aphides were poisoned and the ants who drank their milk were slain. My dairy farm came to a sudden end.

Creation's Doom is a translated book. Consequently criticism that might properly lodge against an author may rightly fall upon the translator. There are any number of statements that sound pretty glib. There is a style that carries the planets into the bosom of the sun. The stream of time is fair enough but "its waves to sweep over the sunken continents of former human achievement" is a bit too undulating for me. Again, "if the cyclops of Greek legend had one eye, man's forerunners had three." Everyone knows that the legend of the cyclops was constructed by the brilliance of Greek imagination from the volcano. If we could stand on the bank of the Nile where the kine in Pharaoh's dream came up out of the river, would we kick out of the depression? The book ails from adjectivitis. I have no quarrel with good sense-impression words, but too much "terror and anguish in the hearts of 10,000 people who watched the catastrophe in the village of Tunguska," Siberia, when the Tunguska meteor fell (July 30, 1908) leaves me thinking that Siberia must have been well settled with villages of ten thousand souls. It is pretty difficult to translate any book and avoid the language carry-over. In Creation's Doom there is a strong German effect. Proper English words have not always been found and the structure often leaves one waiting for the verb.

H. W. ELKINTON.

TAUTOMERISM, by John William Baker, D.Sc., Ph.D. (Lond.) A.R.C.S., F.I.C., 332 pages, illustrations, 14 × 22 cms. New York, D. Van Nostrand Company, Inc., 1934. Price $9.00.

To organic chemists tautomerism is a well-known characteristic of many organic compounds. Even at that, probably relatively few, except the teachers and those deliberately doing tautomeric research, fully realize just how much work and study has been expended upon the subject of this book. Considerable study on tautomeric compounds has been made by several English chemists and the author, J. W. Baker, one who has enjoyed a fairly close contact with such workers, undertakes to bring together and correlate most of the available data.

However, the book is more than a mere compendium of tautomers and their properties. The author utilizes the recent developments of the electronic theory which permits the correlation of tautomeric reactions on a much more fundamental basis than was hitherto possible. The author recognizes that the electronic theory is pretty well accepted on a broad basis although there still is some disagreement as to detail. In order that the subject matter of this monograph shall receive coherent treatment, a single-minded viewpoint has been maintained throughout.

The real introduction to the book is the third chapter, on the Development of the Modern Theory of Tautomeric Change. The tautomers have been arranged in the following classifications: Cationotropic, Dyad, Triad and Pentad, Prototropic, Ring-Chain, Valency, Aniontropic, Transannular and Pinacolic. A worth while supplement to the main text is an appendectical contribution by Prof. C. K. Ingold, F.R.S., who writes on the Significance of Tautomerism and of the Reactions of Aromatic Compounds in the Electronic Theory of Organic Reactions.

T. K. CLEVELAND.

CHEMICAL WAVE TRANSMISSION IN NERVE, by A. V. Hill, F.R.S., Foulerton Research Professor of the Royal Society, Honorary Fellow of King's College, Cambridge, 74 pages, illustrations, 14 × 22.5 cms. New York, The Macmillan Company; Cambridge, University Press, 1932. Price $1.25.

It seems that Professor Liversidge left in his will a bequest to the Master and Fellows of Christ's College, Cambridge, for the encouragement of research in chemistry, particularly research on a subject so vast that many workers shall be necessary and consequently the problem should be as widely publicized as possible. In 1932 the Master and Fellows invited a Physiologist, A. V. Hill, F.R.S., who lectured upon the Chemical Wave Transmission in Nerve. The subject of this Liversidge Lecture forms the context of this book.

Probably no one is better fitted than the author to present such a problem to waiting workers in research. He has labored much himself and realizes better than most what a Herculean task yet remains. The exposition of the problem is excellent. The story begins with a statement of its nature. The velocity of nerve impulses may range from 100 meters per second for a medullated nerve to as low as 0.05 meter per second for a non-medullated variety. This impulse originates in a chemical reaction of some kind. What is this reaction and how it occurs is the problem.

The author carefully and fully describes the structure of nerves; what is at present known regarding the nature of the impulses; and some of the research methods already tried with promising results. The book is supplied with a number of appendices in which several investigative methods are described with considerable technical detail. These include (1) the excitation of nerve, (2) the measurement of the heat production of nerve and (3) the energy of a nerve stimulus.

T. K. CLEVELAND.

A DEMONSTRATION VISUAL TEST, by M. Luckiesh and Frank K. Moss, Lighting Research Laboratory, 26 pages, plates, 15.5 × 23.5 cms, Nela Park, General Electric Company. Price $2.00.

This little volume lends added meaning to the definition of "Seeing: A Partnership of Lighting and Vision." It was the intention of the authors to present a reliable test method which should more or less quantitatively demonstrate the dependence of visibility upon the degree of illumination. As a result of their continuous researches on seeing, they have been able to develop a Demonstration Visual Test which is unique in that it always produces positive results, and at fairly small differences in intensity of illumination. This test consists of letters made by interruptions in very dark gray diagonal lines, the latter being printed on a medium gray. The great lack of contrast was deliberately adopted in order to better illustrate the effects of changes in illumination.

There are five test series. The task is to recognize the capital letter in the center of each pattern and to name it aloud to insure careful performance of the test. The time to perform this series should be recorded. Next, the level of illumination should be changed and experiment repeated with the second series. The difference in time required to perform the two series is a measure of an important effect on seeing produced by the change in level of illumination. The test has been designed for normal vision and inability to distinguish the test-object letters is an indication of subnormal seeing ability.

T. K. CLEVELAND.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

Report No. 485, The Drag of Airplane Wheels, Wheel Fairings, and Landing Gears—I, by William H. Herrnstein, Jr., and David Biermann, 32 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price ten cents.

Tests were made in the 7- by 10-foot wind tunnel and in the 20-foot tunnel of the National Advisory Committee for Aeronautics to determine the drag of a number of airplane wheels, wheel fairings, and landing gears designed or selected for an airplane of 3,000 pounds gross weight. All tests were made on full-sized models; those in the 7- by 10-foot tunnel were made at air speeds up to 80 miles per hour and those in the 20–foot tunnel were made at air speeds up to 100 miles per hour. Although most of the landing-gear tests were made in conjunction with a fuselage and at 0° pitch angle, some of the tests were made in conjunction with the fuselage plus wings and a radial air-cooled engine and at pitch angles from −5° to 6° to obtain an indication of the general effect of these various items on landing-gear drag. All tests were made in the absence of propeller slipstream.

The results of the investigation show that the lowest drag recorded for any landing gear tested was 13 pounds, at 100 miles per hour and 0° pitch, and that it might be possible to reduce this drag approximately 6 pounds by totally encasing the wheels of this gear in fairings. The highest landing-gear drag recorded was 98 pounds. Other points of interest brought out were: Fitting-plus-interference drag of ordinary types of landing gears averages about 44 per cent. of the drag due to these gears; low-pressure wheels and tires may be used with little or no increase in landing-gear drag; the proper wheel fairing may reduce the drag due to a landing gear more than any other refinement; fairing of all struts is of great importance; and landing gears having a single supporting strut have less drag than any other types of nonretracting gears. Also, the substitution of low-drag or retractable landing gears for conventional types on high-drag airplanes results in a negligible increase in high speed. Low-drag or retractable gears used in place of conventional gears on low-drag airplanes result in a substantial increase in high speed or saving in power at the same speed, the low-drag gear accomplishing a large percentage of the gain obtainable from the use of the retractable gear.

Report No. 487, An Aerodynamic Analysis of the Autogiro Rotor with a Comparison Between Calculated and Experimental Results, by John B. Wheatley, 17 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price five cents.

An extension of the autogiro theory of Glauert and Lock is here presented in which the influence of a pitch varying with the blade radius is evaluated and methods of approximating the effect of blade tip losses and the influence of reversed velocities on the retreating blades are developed. The resulting equations have been applied to determine the characteristics of a PCA-2 autogiro rotor. A comparison of calculated and experimental results showed that most of the rotor characteristics could be calculated with reasonable accuracy, and that the type of induced flow assumed has a secondary effect upon the net rotor forces, although the flapping motion is influenced appreciably. An approximate evaluation of the effect of parasite drag on the rotor blades established the importance on including this factor in the analysis.

Report No. 491, Vibration Response of Airplane Structures, by T. Theodorsen and A. G. Gelalles, 22 pages, tables, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price ten cents.

This report presents test results of experiments on the vibration-response characteristics of airplane structures on the ground and in flight. It also gives details regarding the construction and operation of vibration instruments developed by the National Advisory Committee for Aeronautics.

In the ground tests a study was made of the vibration response of the fuselage, wings, and tail by applying sinusoidal forces and couples at different parts of the fuselages of two airplanes. The amplitudes of vibration along the fuselage and wings at various frequencies were measured and plotted, and the important natural modes of vibration were determined.

In the flight tests vibration records were taken in the cockpits and the tails of two airplanes. The vibograms obtained in flight tests were analyzed and the amplitudes of the fundamental frequencies and the most important harmonics were plotted.

Report No. 492, Tests of 16 Related Airfoils at High Speeds, by John Stack and Albert E. von Doenhoff, 23 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price ten cents.

In order to provide information that might lead to the development of better propeller sections, 13 related symmetrical airfoils have been tested in the N.A.C.A. high-speed wind tunnel for a study of the effect of thickness-form on the aerodynamic characteristics.

The thickness-form variables studied were the value of the maximum thickness, the position along the chord at which the maximum thickness occurs, and the value of the leading-edge radius.

The tests were conducted through the low angle-of-attack range for speeds extending from 35 per cent. of that of sound to slightly in excess of the speed at which a compressibility burble, or breakdown of flow, occurs. The corresponding Reynolds Number range is 350,000 to 750,000. Because the Reynolds Number for the tests is somewhat lower than that at which most propellers operate, and much lower than that at which airplane wings operate, the data are not directly applicable to many practical problems, but it is probable that some of the relations shown, particularly the relative effect of the shape changes as affected by compressibility, are valid at much higher values of the Reynolds Number. The results obtained were applied to the design of three cambered airfoils which were tested as part of this investigation.

The principal factors affecting the choice of propeller sections are low drag at low and moderate lift coefficients and a late compressibility burble, that is, low drags at high speeds. Considering these factors, the results indicate that the maximum thickness should be small and located at approximately 40 per cent. of the chord aft of the leading edge. Small variations from the normal values for the leading-edge radius are shown to have small effect on the aerodynamic characteristics. A comparison with similar tests of commonly used propeller sections indicates that at high speeds one of the cambered airfoils tested, the N.A.C.A. 2409–34, is superior. The results also indicate that some further improvement in airfoil shapes for high-speed applications may be expected.

R.

ELECTRONS AT WORK, A SIMPLE AND GENERAL TREATISE ON ELECTRONIC DEVICES, THEIR CIRCUITS, AND INDUSTRIAL USES, by Charles R. Underhill, first edition, 354 pages, tables, illustrations, 15 × 23 cms. New York and London, McGraw-Hill Book Co., Inc., 1933.

During recent years there has been an enormous amount of experimental work and development on the subject of electronic theory that held great promise. That this promise has been well founded is revealed by this book. This subject is a difficult one to treat in the manner here recorded, i.e. to give a clear and brief explanation without going too deeply into theories and technical discussions. That that development has only begun to produce results is very forcefully impressed upon the reader.

The book may be divided into two parts. The first part is devoted to the review and enlightenment on fundamental subjects of physics leading up to the vacuum tube. This includes electrostatic theory, dielectrics and electric condensers, magnetic and electromagnetic effects, alternating currents, and space, time and oscillations. A picture is given of what an electron is and its characteristics. The electrodes in a vacuum tube and their functions during operation are described as well as circuit characteristics and phenomena. The peculiar nature of wave trains of exceedingly high frequencies, resulting from oscillating electrons in atoms striking matter (photoelectric effect) is discussed after which there follows a discussion of types of photoelectric cells.

The second part of this book treats on the many and various uses to which the electron tube can be put. Their application as rectifiers of alternating current, as relays for power circuits, as producers of rays, etc., is treated in detail. It is difficult to read this part without a thought being evolved as to the possibility of more applications of this wonderful little device.

The very nature of this book is such that it should particularly appeal to those having charge of industrial operations, who can appreciate principles and applications rather than present apparatus and equipment which may later be improved. The very good index facilitates reference. It should also appeal to all those having a knowledge of physics as a means of removing the mystery of electronics.

R. H. OPPERMANN.

MODERN PHYSICS, A SECOND COURSE IN COLLEGE PHYSICS, by G. E. M. Jauncey, D.Sc., 568 pages, illustrations, tables, 14.5 × 22.5 cms. New York, D. Van Nostrand Company, Inc., 1932. Price $4.00.

This book is the outgrowth of a series of mimeographed notes first used in a course in modern physics at Washington University in 1929–30, taught by the author. Because of the interest shown by students who were attracted to this course, which required them to continue in physics after the first year, the notes were expanded into the present book and the experience gained in three years of teaching has resulted in considerable modification in selection of subjects.

In discussing the term "Modern Physics" as related to classical physics, the author points out that the most fascinating and interesting parts of physics are those which are either in the process of active formation or which have just recently been developed, but it is essential that a good grounding be had in classical physics in order to appreciate modern physics.

In "Historial Introduction," Chapter 1, facts in history of physics in the days of the Greeks, Romans, Arabs and Middle Ages are brought out in such a way as to associate them with the larger setting of events in world history. Following this is a chapter on useful mathematics for the benefit of the reader who has not had a course in calculus. A knowledge of algebra, trigonometry and geometry is assumed.

The selection of subjects of the following chapters include The Electron, Kinetic Theory of Gases, Thermionics, Photoelectric Effect, Bohr Theory of Spectra, Radio and Television, Geophysics, Astrophysics, and Relativity. Of particular interest is Chapter XXIII on Recent Ideas in Physics. This chapter reviews the quantum theory before 1923, its status in 1923–25, and the new quantum theory. After touching on the Heisenberg Uncertainty Principle in the measuring of the position or velocity of an electron there is brought out briefly some interesting philosophical implications regarding human affairs, namely freedom of will.

At the end of each Chapter there are a number of problems to be worked out by the student. Answers can be found in the back of the book. Appendix I gives table values of e^{-x}.

While the intent of the book is mainly for students, it may be profitably used by graduates of technical schools especially those whose daily occupations carry them into more or less highly specialized fields, and who therefore do not have opportunity to become familiarized with the subjects treated.

R. H. OPPERMANN.

PHYSICS, A TEXTBOOK FOR COLLEGES, by Oscar M. Stewart, Professor of Physics, University of Missouri, revised edition, 770 pages, illustrations, tables, 14.5 × 21.5 cms. Boston, Ginn & Company. Price $4.00.

This revised edition is an excellent text book on elementary physics. The first edition was intended particularly for those who have not had special training in mathematics and the present work, following along the same lines, is outstanding for its simplicity. It would be difficult to find a clearer treatment of the subject.

In Part I the mechanics and properties of matter are covered from force and units of measurement up to the molecular and atomic theory of matter. Part II, on heat, gives attention to temperature and its measurement expansion, transfer of heat, change of state, and heat engines. In this Part, a chapter on meteorology serves to give applications of the principles of physics to phenomena within the understanding of all. Parts III, IV and V, on wave motion and sound, magnetism and electricity, and light, respectively, complete the text. An appendix gives numerical equivalents of length, speed, force, power, etc.

The entire structure of the book spells helpfulness and assistance to the student. The different parts are divided into chapters which are divided again into sections so that segregation of some of the more difficult parts of the subjects treated is possible and the student may study these separately. Summaries are given at the end of each chapter, as are problems, the answers to the more difficult being given in the appendix.

R. H. OPPERMANN.

MODERN THERMODYNAMICS BY THE METHODS OF WILLARD GIBBS, by E. A. Guggenheim, M.A., with a Preface by F. G. Donnan, 206 pages, diagrams, 14.5 × 23 cms. London, Methuen & Co., Ltd. New York, E. P. Dutton & Co., Inc. 1933.

In the Preface, F. G. Donnan states that the author has undertaken to give, in the present work, an exact and yet very compendious account of thermodynamics as was conceived by J. Willard Gibbs in his famous paper on "The Equilibrium of Heterogeneous Substances."

The author states in his Preface that he has tried to bring out the two most valuable characteristic features of the Gibbs' method which are completely absent from most text books. The first is the use of exact straightforward analytical method instead of cycles which in almost all cases are either simple but inexact or exact but complicated. The second is the use of the "chemical potentials." These play the same fundamental part in determining chemical equilibria as does the temperature in determining mechanical equilibrium.

An important part of the book is the chapters devoted to solutions wherein the author divides solutions into three classes, ideal, semi-ideal and non-ideal. This is a valuable contribution to the study of that branch of physical chemistry. In Chapter X, "Electro-Chemical Systems," it is shown how to avoid the use of functions which are not thermodynamically defined and in Chapter XII, "Surface Phases," attention is given to extent, composition, energy, tension, and equilibrium. A section of this chapter treats on surface phases of a different type than those of Gibbs, those of later scientists which were concerned with the behavior of minute quantities of various substances at the surface of a single underlying liquid, usually water, the substances being so slightly soluble in the liquid phase and so involatile that during the time of an experiment the quantity that can dissolve or evaporate is quite negligible compared with the quantity that remains at the surface.

The book is undoubtedly a great work, one which should be appreciated by all those qualified to absorb its explanations. The notes and references given at the end of each chapter offer much help for further searches on the subject matter treated.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

Atomic Structure and Spectral Lines, by Arnold Sommerfeld, translated from the fifth German edition by Henry L. Brose, vol. 1, 675 pages, illustrations, 14 × 22.5 cms. New York, E. P. Dutton & Co., Inc., Price $10.80.

The Search for Truth, by Eric Temple Bell, 279 pages, 15 × 22.5 cms. Baltimore, The Williams and Wilkins Co., 1934. Price $3.00.

U. S. Bureau of Mines, Minerals Yearbook, 1934, 1154 pages, tables, 15 × 23.5 cms. Washington, Government Printing Office, 1934. Price $1.75.

Canada, Dominion Bureau of Statistics, Statistics of Steam Railways of Canada for the year ended December 31, 1933, 195 pages, tables, 16.5 × 25 cms. Ottawa, King's Printer, 1934. Price fifty cents.

Canada, Department of Mines, Investigations in Ore Dressing and Metallurgy,

January to June 1933, 157 pages, tables, plates, 16.5 × 25 cms. Ottawa, King's Printer, 1934.

U. S. Coast and Geodetic Survey, First-Order Triangulation and Traverse in Louisiana (1927 Datum), by O. P. Sutherland, 169 pages, tables, maps, 15 × 23.5 cms. Washington, Government Printing Office, 1934. Price fifteen cents.

Bell Telephone Laboratories, Monographs: B-809, Overvoltages on Transmission Lines, by C. L. Gilkeson and P. A. Jeanne, 24 pages, tables, illustrations. B-810, Some Contemporary Advances in Physics—XXVIII, the Nucleus—III, by Karl K. Darrow, 48 pages, illustrations. B-811, Systems for Wide-Band Transmission Over Coaxial Lines, by L. Espenschied and M. E. Strieby, 26 pages, illustrations. B-812, Extension of the Theory of Three-Electrode Vacuum Tube Circuits, by S. A. Levin and Liss C. Peterson, 9 pages, illustrations. B-813. Fluctuation Noise in Vacuum Tubes, by G. L. Pearson, 20 pages, illustrations, B-814, Measurement and Reduction of Microphonic Noise in Vacuum Tubes, by D. B. Penick, 20 pages, tables, diagrams. B-815, Regeneration Theory and Experiment, by E. Peterson, J. G. Kreer, and L. A. Ware, 21 pages, illustrations. B-816, Electromagnetic Theory of Coaxial Transmission Lines and Cylindrical Shields, by S. A. Schelkunoff, 48 pages, tables, 8 pamphlets, 15 × 23 cms. New York, Bell Laboratories, 1934.

National Advisory Committee for Aeronautics, Technical Notes, No. 508, Landing Characteristics of an Autogiro, by William C. Peck, 8 pages, tables, 20 × 26 cms. Washington, Committee, 1934. No. 509, Tank Tests of Flat and V-Bottom Planing Surfaces, by James M. Shoemaker, 25 pages, tables, figures, 20 × 26 cms. Washington, Committee, 1934. No. 510, The Calculated Effect of Trailing-Edge Flaps on the Take-Off of Flying Boats, by J. B. Parkinson and J. W. Bell, 15 pages, tables, 20 × 26 cms. Washington, Committee 1934. No. 511, A Study of the Pitching Moments and the Stability Characteristics of Monoplanes, by George J. Higgins, 16 pages, figures, 20 × 26 cms. Washington, Committee, 1934.

CURRENT TOPICS.

Chemistry in Archæology.—(*Chem. & Ind.*, 53, 736.) From time to time an interesting item will appear telling how some controversial point in archæological research has been cleared up by the aid of chemistry. It is somewhat like eating a multi-course meal with each course a dessert, to read H. W. BASSETT'S paper: "Chemistry as the Handmaid of Archæology." Here, in rapid succession, facts concerning the origins of many arts are given as evidence of chemistry's ability to unlock riddles older than the Sphinx.

Gold.—Bright lumps of this native metal could not have failed to attract primitive man. Too soft for tools, the metal was shaped into ornaments. Only when gold was found naturally alloyed with metals which hardened it could it be used for other purposes. Thus, the aboriginal inhabitants of Brazil made their fishhooks of gold alloyed with 19.5 per cent. copper and 1.5 per cent. platinum. Gold found with early dynasty remains in Egypt contained silver in considerable proportion while later period specimens were found to be debased with copper.

Copper.—The discovery of copper initiated the change-over from tools of stone to those of metal. Objects of hammered copper have been found among the Chaldean remains which go back as far as 4500 B.C. Analyses of copper articles found in Egypt show less than 0.5 per cent. of tin, of arsenic and of iron. Some were found to contain small quantities of antimony, bismuth, zinc and lead. Copper strip taken from a sarcophagus of the Twelfth Dynasty (2000–1788 B.C.) was found to contain more than 4 per cent. of arsenic.

There is a tradition that Egyptians hardened copper by quenching when red hot in ox blood. Cooling in this way, hardens steel but softens copper. If any appreciable degree of hardening exists it is due to an alloy of copper with some other metal or metalloid. When corroded copper objects cannot be told from bronze, only a chemical analysis will ensure identity which in turn aids greatly in dating the object, since bronze was introduced a number of centuries after copper. Probably the production of bronze by the addition of 12 per cent. or less of tin was purely accidental. Tin as such was not known, but only that its ore, when mixed with the ore of copper before smelting, produced a bronze.

Brass is another alloy of copper, in which zinc is the chief constituent. The earliest known brass relics were found in the ruins of the city of Kameiros in Rhodes, which was destroyed in the sixth century B.C. Very little brass was used in Egypt, though specimens have been found. Zinc was not known as such until the sixteenth century A.D. in Europe.

Iron.—This element of such modern importance occurs so infrequently in its native state that methods for its production were learned only long after that of gold and copper. Probably iron made from ore (as distinct from meteoric iron) was not fabricated in quantity prior to about 1350 B.C. Iron beads of the Egyptian pre-dynastic era were found completely converted into oxide. Undoubtedly these were of meteoric origin. Prior to the Roman invasion of Britain there was a monetary system in force in which currency bars of iron were used.

Metallurgical Lore.—The method of making metal articles by spinning from sheets or discs probably was not known in Egypt prior to 30 B.C. Close examination of specimens of copper work show that prior to 2000 B.C. the art of annealing at least was not practiced in Egypt up to that time. On the other hand, micro-examination of a knife-blade or spear found in the royal graves of Ur dated about 2700–2600 B.C. showed the metal to have been worked and annealed. Absolutely no evidence has been discovered for the claim that many Egyptian metal objects were formed by welding.

Lead.—Very old lead articles have been found in Egypt, but they were few in number. Leaden objects were uncovered at Nineveh having been used by the Assyrians about 900 B.C. Not until 700 years later was lead intentionally added to copper to render it more fluid when casting. The best examples of Egyptian lead work date from Ptolmaic and Roman times. These are head-dresses for use on statues. Some parts were cast direct while others were beaten into shape. Lead pigs made by the Romans shortly after invading Britain were found marked "Ex. Arg." indicating that the lead had been desilverized. The Romans also were responsible for the first known pewter, an alloy of lead and tin. A fragment of a coffin taken from a Roman cemetery was examined spectroscopically and found to be an alloy of approximately 95 per cent. lead and 5 per cent. tin, the metals being remarkably pure. Antimony was the only impurity present in an appreciable amount and that was no more than 0.5 per cent. Only the merest trace of silver was present. Antimony beads dating from the Twenty-second Dynasty have been found in Egypt. Since this metal does not occur there in any form, these beads must have been imported.

Embalming.—The ancient Egyptians embalmed their dead, the chief reason appearing to be that if the body were kept life-like in appearance the soul would stay near it, and would not begin to wander away so soon. Three methods were used, the most expensive costing about $1250 of our money today. Part of the brains was drawn out through the nostrils by an iron hook, and the remainder disposed of by an injection of drugs. An incision was made in the side of the abdomen and the bowels removed. These were placed in a chest and cast into the Nile following the saying of prayers by the embalmer-priests. The abdomen was then washed with palm wine and filled with myrrh, cassia, and spices, and the body placed in a bath of natrum and steeped for 70 days. After steeping, the body was removed, allowed to drain, and the eyes, mouth, nose and embalming incision filled with beeswax. The wrapping, invariably done by the relatives, consisted of linen bandages fastened with gum arabic.

Second class embalming cost about one-third as much and was much simpler. No incision was made, and the body was filled with "oil made from cedar." The body was steeped in natrum though not for so long. On the last day, the "oil of cedar" was allowed to run out of the body, when it brought with it all the intestines and vital organs, which had liquefied. This so-called natrum is a natural soda found in Egypt and consists essentially of carbonate and bicarbonate. Frequently it is contaminated with salt, and the preservative value of this was fully experienced in the cheapest method of embalming where the body was simply soaked in a solution for several days. There is little or no evidence that bitumen was used in embalming despite the black appearance of many mummies.

C.

A Unique Water Supply.—(*Chem. & Ind.*, **53**, 819.) Geologists find that at present the islands of Bermuda consist essentially of coral rock or of sand consolidated from the coral growth of countless years, to a depth of 100 feet or more below sea level. Because of the porous nature of the substratum, the islands are therefore saturated from one side to the other and from end to end by salt sea water at the existing sea level. Obviously any well drilled vertically downward would pass first through porous coral sandstone and eventually into the salt water permeating this coral sand stone.

PROF. W. D. TURNER points out that Bermudians, therefore, have learned to depend on rain water for their carefully conserved fresh potable supply. In times of long-continued droughts these

sources naturally become depleted and the shortage has been obviated only in part by importation of fresh water as ballast from New York.

The total annual rainfall, however, is somewhere between 40 and 60 inches and water engineers have asked why an appreciable quantity of this fresh water cannot be intercepted in its percolating course downward to mix with the salt water. Since the fresh water is lower in gravity it will not sink through the salt but will flow laterally in either direction toward sea level. The natural resistance to flow set up by the soil will cause a hydrostatic head to build the water in a lens-shaped stratum higher in the middle and tapering down to sea level at the edges. If means can be found to tap this fresh-water lens without disturbing the salt water table below, then fresh water should be secured.

Such a project was found to be entirely possible. To tap this water it was necessary to excavate a trench down to the fresh-water lens, then through the thin edge of this lens to within a few inches of the sea-water level. A 400-foot trench was constructed so that it intercepted the fresh-water lens for a depth of about 18 inches and with the trench bottom still 6 inches above sea level. During the excavation thousands of tiny springs began to run at once into the trench, some even as large as 2 inches in diameter. The water thus collected by the trench was diverted to a central pumping well through an open-joint tile line. These open joints in the tile pipe were carefully covered with coarse rock, after which the entire trench was back-filled and closely packed with coral sand. This fill, about 4 feet in depth, acted to cause surface water to flow over the top of the trench.

An analysis of the water collected in this horizontal well indicated a salt content, expressed as sodium chloride, of about 80 parts per million. During a three-months test period this salt content never fluctuated more than 20 parts above or below this figure. The hardness of the water was found to be upwards of 250 parts per million, expressed as calcium carbonate. Softening and chlorinating equipment have been installed and the system in its present form is capable of delivering a pure, fresh, soft water at the rate of seven million gallons per month.

C.

Recent Developments in Atomic Physics.—(*Science Service.*) DR. ENRICO FERMI bombarded uranium with non-electrical particles known as neutrons and believes he has created the super-heavy element No. 93. There is plenty of controversy in scientific circles

over whether such is the case. Now Dr. Fermi has bombarded the element thorium in a similar manner and discovered two radioactive substances of thorium having periods of one and fifteen minutes during which they disintegrate to half their amount. These new products would be classed as isotopes of thorium or actinium.

* * * * *

A paradoxical action of gamma rays was reported by DR. R. A. MILLIKAN at the International Conference of Physics. He and his colleagues found that the higher the energy of a gamma ray the more it is absorbed. A record was made when the maximum energy of the gamma rays was measured as between twelve to thirteen million electron-volts.

* * * * *

PROF. J. JOLIOT and his wife, the former Irene Curie, predict the artificial production of radioactive elements superior in intensity to radium and exceedingly useful in medicine. A very important characteristic of these new active elements is that when introduced into the body they will disintegrate without leaving a radio-active residue. Thus a new kind of cancer treatment is forecast, in which artificial radioactive substances produced cheaply can be introduced directly into the cancerous tissue to do their work and then become harmless.

* * * * *

PROF. M. L. OLIPHANT, of the Cavendish Laboratory, Cambridge, reports the production of a new kind of helium of atomic weight six instead of the usual four. This new variety of helium was obtained by bombarding beryllium with deutons, the hearts of double-weight hydrogen.

C.

Carbon Copies by Radio.—(*Science Service.*) According to CHARLES J. YOUNG, speaking before the Institute of Radio Engineers, the day is not far off when messages in facsimile shall be transmitted by radio. Thus, messages typed or written in long hand will be received in an identical condition. Whole pages of a newspaper could be sent in this manner.

By this method of radio transmission one actually receives a carbon copy of the original message, at the transmitting end the apparatus "scans" the message with a photoelectric cell. The

current variations so produced are sent out in the form of a radio signal. At the receiving end the recorder is essentially a small spiral of wire against which runs a sheet of carbon paper, backed by white paper. The variations in blackness of the original message are reproduced by the degree with which the wire presses against the carbon paper and creates marks on the white paper beneath it. Each minute one and two-tenths inches of the original document can be reproduced thousands of miles away.

C.

A Rubber Rival of Cellophane.—(*Science Service.*) Pliofilm is the name of a new transparent and water proof wrapping material. This new rival of cellophane is produced synthetically from rubber by processes requiring the same careful control given to cellulose products. A noteworthy characteristic of pliofilm is the retention of its moisture-proofness on wrinkling, creasing and related types of abuse that reduce or eliminate the effectiveness of most other "moisture-proof" wrappers in practical use. It does not have the stretchable elasticity one thinks of in connection with rubber, but rather a toughness, with some "give." The "heat sealing" properties of Pliofilm are a distinct advantage. Only moderate heat and pressure are required for producing a strong, permanent seal of two edges.

C.

Age and Vitality of Seeds.—According to EDGAR BROWN, in charge of the Division of Seed Investigations, the vitality of any seed cannot be stated in terms of age. In general, older seeds do not germinate so well as fresh seeds. Seed deteriorates more rapidly where the climate is warm and moist than where it is cool and dry. Much also depends upon the quality of the seed crop in any given year. Thus, seeds of different field crops were collected for a series of years and stored under identical conditions when tested in 1920 it was found that alsike clover seed from the 1915 crop germinated only 62 per cent. while seed from the 1910 crop has 90 per cent. germination. But germination from the 1911 crop, one year later, was only 13 per cent.

There are not authenticated cases, according to Mr. Brown, in which seed from ancient tombs has germinated, provided the seed is as old as the tomb. So-called "mummy" wheat, dug up by the tourists themselves, has germinated but there is strong evidence that such grain had been placed there recently as bait for the gullible.

The best proof that very old seed will not grow is that chemical change is gradually taking place in all seed, the starches and proteins breaking down through oxidation. Few seeds of any field crops have been found to germinate after 30 years.

C.

A Warning to Takers of Cincophen and Amidopyrine.—Cincophen, a chemical anodyne and sedative, is sometimes used by sufferers from neuralgia, rheumatic pains, neuritis and similar conditions. Amidopyrine is frequently found in headache remedies and other pain killers. Says W. G. Campbell, Chief of the Food and Drug Administration: "The gradual development of serious poisoning from the use of these drugs is often so insidious that the danger is not recognized by the user. Cincophen causes a degeneration of the liver cells. Amidopyrine may cause a reduction in the number of white blood cells, a condition called agranulocytosis.

C.

Glass-Topped Tin Cans.—(*Science Service.*) Tin cans now can be furnished with glass tops in order that the contents may be effectively displayed. Because of the low expansion of the glass when heated it is possible to solder the tin can on to the glass without need for a close-fitting gasket. So strong is the glass-to-tin joint that in tests the glass breaks before it will separate from the tin. In the food processing it is often necessary to place the filled can in a steam autoclave and suddenly cool it with water to prevent overcooking. The special glass resists, satisfactorily, this drastic treatment.

C.

Giant Diesel Locomotives.—(*Science Service.*) CHARLES F. KETTERING, speaking before the National Academy of Sciences, predicted the early appearance of 3600 horsepower diesel-electric locomotives which have four times the power of a similar engine in the now famous Union Pacific streamlined train. They will operate with an efficiency of 36 per cent., equivalent to that of the steam turbines used in large stationary electric generating stations.

The principal trick in making such large diesels lies in the method of injecting the oil fuel into the cylinder where the heat of compressing the mixed vaporized fuel and air explodes the mixture without the aid of a spark, necessary in the gasoline engine. These new diesels use injection pressures fivefold those used in the older types, 25,000 instead of 3000 pounds per square inch. No matter what

the viscosity of the oil used, enough pressure can be applied to break it up into fine vapor through ten-thousandth-inch holes.

C.

Mercury Pressure Lamps.—Characteristics of the high pressure mercury lamp are quite different from the lamps that have heretofore used mercury vapor, because the higher temperature of operation and high mercury pressure give the light a color more like that of the blue sky. In addition, these new lamps produce almost twice as much light for the same power consumption. They operate at an efficiency of 35 to 45 lumens per watt as compared to an efficiency of 15 to 20 lumens per watt for present mercury lamps.

C.

Calcium.—(C. L. MANTELL AND CHARLES HARDY, *Chem. Industries*, 35, 403.) Calcium, an uncommon metal, is produced by the electrolysis of fused calcium chloride. The commercial method uses a vertical contact cathode upon which the calcium is deposited as the electrode is continuously moved upward. The electrolyte is pure calcium chloride kept at 780° to 800° C. Once in operation, the cathode is effectively one of calcium metal. Thin layers of calcium chloride protect the metal from the air.

Laboratory applications of calcium metal are well known. It is used in freeing absolute alcohol from the last traces of water, by first digesting with calcium turnings then distilling. Calcium also is useful in the production of high vacua. If the metal be heated in a tube connected with a vessel at low pressure, it takes up the last traces of air, forming oxides and nitrides, thereby reducing the pressure in the system to very low values. Calcium does not react with that rare gas, argon, and therefore is employed to separate it from nitrogen.

The number of industrial applications for calcium has increased rapidly in recent years. Three to four-hundredths per cent. added to lead greatly increases the latter's tensile strength and resistance to deformation. Lead so treated should be well suited for sheathing electric cables. Calcium's value as a deoxidizer for copper is now well established. It is preferred to silicon in that it alters the conductivity very little, while silicon affects it markedly. High-calcium copper alloys are now commercially available, usually in powder form.

Calcium added to cast iron to the extent of 0.5 per cent. produces a casting that is denser and more uniform in grain structure. Good results have been obtained with steel. It has the advantages

over other deoxidizers that practically none of the reagent is left in the metal. Methods had to be developed for introducing the calcium metal into the steel. Mechanisms are now used by means of which slugs or pieces of calcium are shot into the ladle of molten metal through an air-pressure gun. There is sufficient force to shoot the calcium projectile deep into the metal where it disintegrates, does its deoxidizing and is converted into lime which rapidly rises to the slag. At the present time slugs can be shot at the rate of 120 to 150 per minute when the gun is hand operated, or 200 to 300 per minute if it is motor driven, and a 60-ton ladle of steel deoxidized in a period of approximately 5 minutes when 2 lbs. of calcium per ton of steel is used.

The price of calcium, which some 15 years ago was still in the neighborhood of $20 per pound, is now less than $1.50. This price represents metal 98.5 to 99 per cent. pure.

C.

Plants That Build on Sand.—After seven months searching the deserts and foothills of Russian Turkistan and most of Turkey for plants to control soil erosion, H. L. WESTOVER AND C. R. ENLOW, plant explorers of the U. S. Department of Agriculture, have returned with nearly 1800 lots of seed. Most of the seed collections represent grasses or legumes which form a thick turf close to the ground, enabling them to bind the soil and hold it against the ravages of wind and water.

One of the most promising collections is seed of a bunch grass, *Aristida pennata*, which grows in scattering clumps in the dry, wind-swept sands of the Kara Kum Desert. It will take root in moving sand, and when the winds become too strong this grass, through its ability to "land on its feet," may be blown for considerable distances and take root where it lands. If it will grow in this country it should be extremely valuable in regions where there are sand dunes.

Another unusual plant is *Carex physoides*, a perennial sedge used extensively for grazing in the Kara Kum Desert of Turkistan. Roots were collected in June and arrived in this country about the first of October. They were planted in a greenhouse in Washington after four months of remaining entirely dry and are now showing signs of growth.

C.

How Little Radium Is Too Much?—(U. S. D. A. Clip Sheet No. 859.) The Federal Food and Drug Administration has the task of

deciding just how much radium is reasonable and allowable as a constituent of a bath salt to be used medicinally. Although a decision has not been made as yet, nevertheless a recent shipment of bath salt from France was not permitted to enter the United States because of its high radium content. In fact, there was eight-billionths of an ounce of radium in a pound of the salts. Too much they say. How was it known there was that much radium present? A gamma-ray electroscope will determine that and even still smaller quantities.

C.

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